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THE ADSORPTION OF CAUSTIC SODA BY CELLULOSE

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We have shown (1) that purified cotton will take up about 27 per cent of water from saturated water vapor at 25°C. when equilibrium is approached from both sides. Other investigators have approached the equilibrium only from the lower side and have obtained values of from 21 to 24 per cent. Leighton (11) tried to reach equilibrium from the upper end by using a slow-running centrifuge, and calculated that about 400 per cent of water was retained by the cotton. Coward and Spencer (5) used a more effective centrifuge, and reported that about 50 per cent of water was retained. We used a modified Foerst centrifuge and got the water content down to about 10 per cent, with no certainty that we could not have gone lower with a more effective centrifuge. Consequently, it is possible to remove some of the adsorbed water or adsorbed solution by sufficiently effective centrifuging. One must therefore obtain in each case some method of recognizing at exactly what point all of the unadsorbed solution or mother liquor has been removed.

When studying the adsorption of caustic soda from aqueous solution by cellulose, Vieweg (15) used a method depending on the change in concentration of the solution before and after the cellulose was added. This change-in-titer method has been used by practically everyone else, except Leighton, Coward, and Spencer, and ourselves (2). A known amount of a known concentration of caustic soda is shaken with cellulose. When equilibrium is reached, a measured quantity of the supernatant liquid is pipetted off and titrated for caustic soda. From the change in titer it is possible to calculate the amount of caustic soda adsorbed, provided no water is taken up, but not otherwise. Calkin has shown that the true equation for the adsorption is

$$\frac{G(X_0-X)}{S}+\frac{XB}{S}=\frac{A}{S}$$

Here G = grams of solvent (water) in caustic soda solution at the start.
X_0 = moles of caustic soda per gram of solvent at the start.
X = moles of caustic soda per gram of solvent in the supernatant liquid when equilibrium is reached.

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[1] Fellow, The Textile Foundation.

A = moles of caustic soda taken up by the sample of cellulose.
B = grams of solvent (water) taken up by sample of cellulose when equilibrium is reached.
S = grams of cellulose in sample.

Analytically, the material adsorbed in cases of positive adsorption may be considered as adsorbed solution plus excess of adsorbed solute. In Calkin's equation $G(X_0 - X)/S$ represents the excess solute and XB/S represents adsorbed solution. If no water is taken up, $B = 0$ and the first term of the equation gives the true adsorption. This is the value given by the change-in-titer method. If the solution is adsorbed without change, $G(X_0 - X)/S = 0$. These are the two limiting cases, and this was pointed out in words, though not algebraically, by Leighton nineteen years ago. It is understood by colloid chemists, but is still a closed book to most cellulose chemists, especially the German ones.

Whenever water is adsorbed, as is the case with cellulose, the problem is to determine the term XB/S. If we could pipette off and weigh the whole of the mother liquor, an analysis of that or of the residue would give us the answer. We cannot do this directly and must therefore devise an indirect method.

The situation and the remedy are shown graphically in figure 1, which is not to scale. The abscissas represent at will grams of water per gram of cotton in the system or grams of water per gram of cotton in the adsorbing phase. The ordinates are the corresponding values for grams of caustic soda per gram of cotton. Suppose we start with 100 g. of such a caustic soda solution plus such an amount of cotton that the amounts of water and caustic soda are represented by *F* in figure 1. After equilibrium is reached a measured amount of solution is pipetted off and titrated. This gives a ratio of caustic soda to water represented by some point on the line *OH*, but we do not know where on that line because we only determine the ratio of caustic soda to water and we do not know how much caustic soda or how much water there is in the total mother liquor. If we make the assumption involved in the change-of-titer method, that no water is taken up by the cotton, then the point is at *H* where the line *OH* meets the perpendicular from *F*. The amount of caustic soda adsorbed is given by the distance *FH*.

If the true position of the point is at *D*, for instance, the amount of caustic soda adsorbed is *FE* and of water adsorbed is *DE*. Our problem is to locate *D*. The simplest way theoretically would be to centrifuge the system and to analyze the centrifuged solution from time to time. As long as only mother liquor is coming off, the composition will remain constant and will be represented by an unknown point on *OH*. As soon as the composition changes, we know that some adsorbed solution is coming off.

Analysis of the residual mass in the centrifuge at this moment will give the true adsorption, provided no cotton has been lost.

This was not practical with our centrifuge because the centrifuged liquid spattered a good deal and because the final amount to be driven off might be so small as to make the errors of analysis large. Another method was therefore tried. Going back to figure 1, we draw *F′D′* and *E′D′* such that *OF′* = *DE* and *OE′* = *FE*. *D′* is then the composition of the cellulose phase in equilibrium with a cellulose-free, caustic soda solution whose composition is given by the line *OH*. If we centrifuge the original system for different lengths of time and analyze the residual masses, we shall get points on *FD′* so long as we are removing mother liquor only. After we pass *D′*, the resulting points will lie somewhere in the rectangle *D′E′OF′*. If the adsorbed solution goes off without change we shall pass along *D′O*. If only water goes off, we shall get the line *D′E′*. If only caustic soda we shall get the line *D′F′*. Those are the three limiting cases. The point *D′* comes where the straight line *FD′* breaks. From the observed points on *FD′* and beyond, we can calculate the composition of the coëxisting

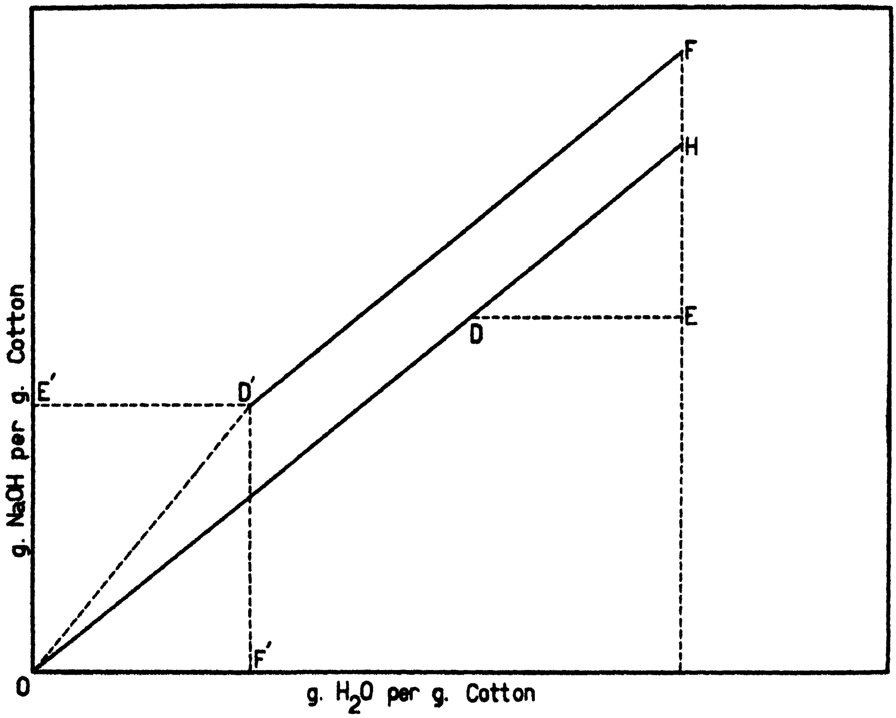

Fig. 1. Determination of True and Apparent Adsorption

solution. So long as the calculated composition remains constant and corresponds to a point on *OH*, only mother liquor is coming off. The change from the constant value indicates that the system is passing through *D'*. This is the method that we have found most successful. The data for one run are given in table 1.

The cotton used in these experiments (4) was "standard cotton cellulose." The data shown in figure 5 were obtained with Johnson and Johnson absorbent cotton purified somewhat less rigorously. One hundred grams of cotton was placed in the A.C.S. apparatus and the cotton was steeped in a boiling solution of 1 per cent sodium hydroxide for $1\frac{3}{4}$ hours, after which it was washed by the A.C.S. method. The amount of cotton in the centrifuge was about 0.5 g.

TABLE 1

Determination of true adsorption by cotton

TIME OF CENTRIFUGING	CENTRIFUGED COTTON		CENTRIFUGED LIQUID BY DIFFERENCE		CENTRIFUGED LIQUID
	NaOH per gram of cotton	H_2O per gram of cotton	NaOH	H_2O	NaOH PER GRAM OF H_2O
Initial concentration: 3.5971 g. of NaOH per gram of cotton, 18.379 g. of H_2O per gram of cotton					
minutes	*grams*	*grams*	*grams*	*grams*	*grams*
0	Solution in equilibrium with cotton				0.18832
$\frac{1}{4}$	0.5435	2.169	3.0536	16 210	0.18838
$\frac{1}{2}$	0.5315	2.099	3.0656	16.280	0 1883
1	0.5172	2.013	3 0799	16.366	0 18819
3	0.5108	1.983	3 0863	16.416	0 1880
Assumed initial concentration: 0.7008 g. of NaOH per gram of cotton, 3 000 g. of H_2O per gram of cotton					
minutes	*grams*	*grams*	*grams*	*grams*	*grams*
0	Solution in equilibrium with cotton				0.18832
$\frac{1}{4}$	0.5435	2.169	0.1573	0.831	0.1893
$\frac{1}{2}$	0.5315	2.099	0.1693	0.901	0.1879
1	0.5172	2.013	0.1836	0.987	0.1860
3	0.5108	1.963	0.1900	1.037	0.1833

The values entitled "Centrifuged liquid by difference" in the fourth and fifth columns are obtained by subtracting the values entitled "Centrifuged cotton" in the second and third columns from the corresponding concentrations given under "Initial concentration" and "Assumed initial concentration." The value given under "Solution in equilibrium with cotton" is a direct determination.

The break comes at about the half-minute observation. It can be made more sharp by starting with a system containing much less supernatant liquid. One could pour off as much of the supernatant liquid as possible, weigh and analyze it, and calculate the filtered residue. We have taken arbitrarily a point on *FD′*, figure 1, which we knew to be short of *D′*. The calculations in the lower half of table 1 are based on these values.

Another way of emphasizing the break is to calculate the apparent or change-in-titer adsorption, which is the amount of caustic soda adsorbed in excess of that due to adsorbed solution. For this particular case, we find 136, 135, 136, 138, and 141 mg. of sodium hydroxide per gram of cotton for 0, $\frac{1}{4}$, $\frac{1}{2}$, 1, and 3 minutes centrifuging, respectively. For an entirely different initial solution the values were 27.9, 27.4, 27.9, and 29.2 for $\frac{1}{2}$, 1, 3, and 5 minutes centrifuging, respectively. Here the break comes after the three minutes centrifuging.

TABLE 2

True adsorptions of sodium hydroxide and water by cotton

MOLALITY OF END SOLUTION	ADSORPTION PER GRAM OF COTTON	
	NaOH	H_2O
M	*grams*	*grams*
1.741	0.0767	0.701
3.421	0.3573	1.914
4.040	0.4938*	2.290*
4.708	0.5315	2.099
5.923	0.5923	1.894

* The quarter-minute centrifuging was too long, so these points have been obtained by extrapolation.

For this work it would be better to have a variable-speed motor to drive the centrifuge, as Coward and Spencer did. On a half-minute run there might easily be errors due to inadequate time for diffusion.

Similar runs have been made for other initial concentrations. The calculated values for the true adsorptions are given in table 2 and figure 2.

The abscissas in figure 2 are molalities of caustic soda in the solution in equilibrium with cotton. The bottom curve represents the apparent adsorption for caustic as given by the change-in-titer method. For 6 molal caustic soda the apparent adsorption is about 0.6 mole of caustic soda per mole (162 g.) of cotton, while the real adsorption is about 2.4 moles of caustic soda per mole of cellulose, an increase of approximately 300 per cent. As had been found by Leighton and by Coward and Spencer, the amount of water taken up by the cotton first increases with increasing caustic soda and then passes through a maximum. The curve for adsorbed caustic soda is smooth and shows no signs of the occurrence in mass of any definite chemical compound in stoichiometric proportions between caustic soda and cellulose.

The general relations are shown in figure 3, where the ends of the dotted lines show the compositions of the caustic soda solutions in equilibrium with the cotton. The solid curve gives the true adsorptions expressed in grams of cotton, water and caustic soda equalling 100. The apparent or change-in-titer adsorption curve would be at the real bottom of the diagram, on the line connecting 100 g. of cotton with 100 g. of caustic soda. Our value of 27 per cent water taken up by cotton becomes 21.2 when plotted in the triangular diagram.

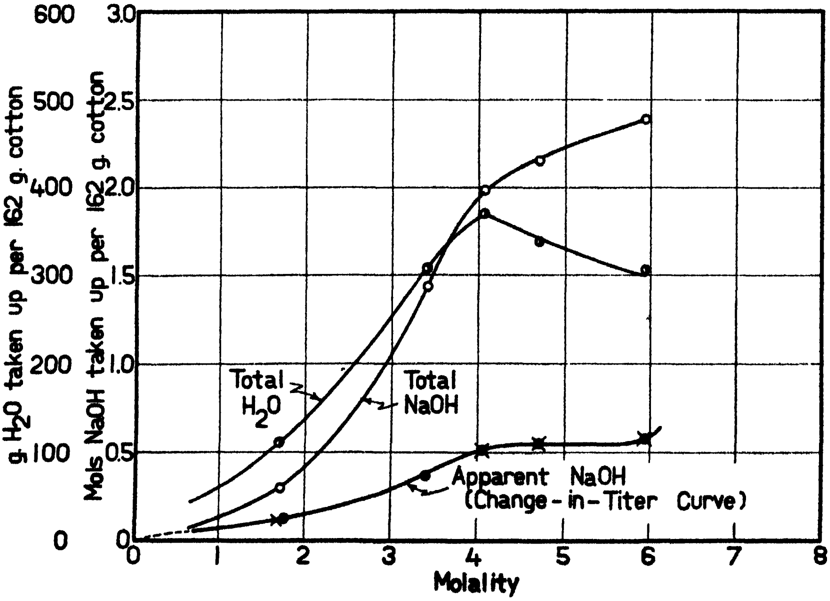

FIG. 2. SODIUM HYDROXIDE AND WATER TAKEN UP BY COTTON

Even if the change-in-titer method gave true adsorptions instead of containing errors of 300 per cent or so, the data would not justify the conclusions that the German chemists draw from them. In figure 4 is given a compilation made by D'Ans and Jaeger (6) of results obtained by Vieweg (15), Karrer and Nishida (10), Rassow and Wadewitz (13), Heuser and Niethammer (8), Heuser and Bartunek (9), Dehnert and König (7), and Liepatoff (12). With the concentration plotted along the abscissas, the presence of two solid phases would show itself by a vertical portion of the curve. There is no evidence of any such thing on any curve except that by Liepatoff, and the vertical portion of his curve ends at nearly 200 mg. of sodium hydroxide taken up per gram of cellulose instead of about 116 mg. of sodium hydroxide, which would correspond to $(C_6H_{10}O_5)_2 \cdot NaOH$.

That these data should be so divergent is quite natural in view of the results recorded in figure 5, showing the effect of the previous history of the cotton.

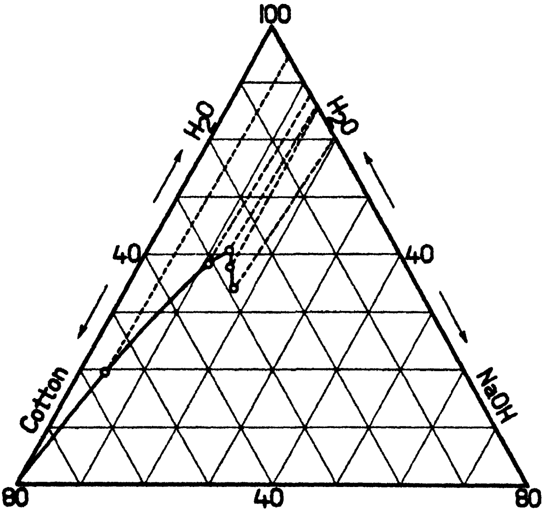

FIG. 3. SODIUM HYDROXIDE AND WATER TAKEN UP BY COTTON

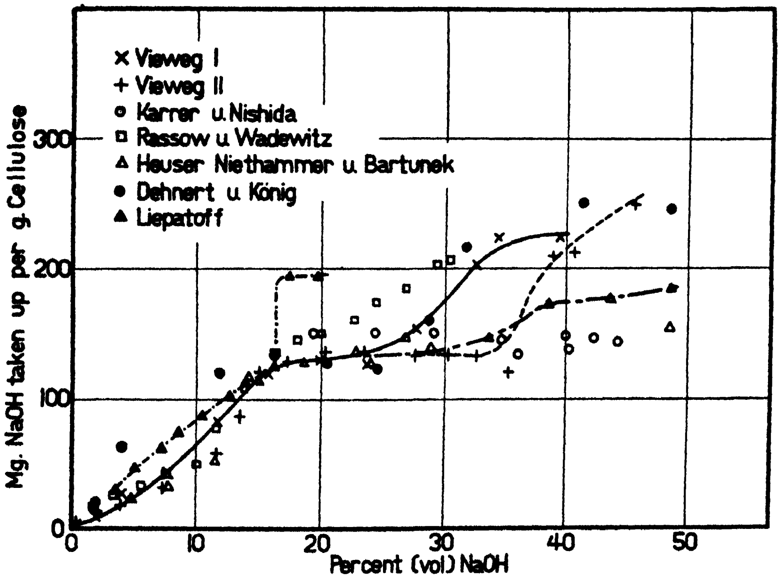

FIG. 4. SODIUM HYDROXIDE TAKEN UP BY CHANGE-IN-TITER METHOD

The table references are to the paper of Bancroft and Calkin (2). By working judiciously one can get almost any value of the adsorption that one wishes; if one works injudiciously, as most people have done, the sky is the limit. The interesting thing for the moment is that the arrows show that one does not pass back along the same curve if one washes out the caustic soda, except for very low initial concentrations. The cotton behaves toward caustic soda as silicic acid does toward water. In our experiments the different up-curves came together at about 4 molal caustic soda or at about 14 per cent caustic soda; this is about the concentration at which the x-ray analysis for ramie (14) shows that the change from one space lattice to another is complete. Change from one space lattice to another would be expected to change the degree of adsorption, and apparently it does. This is not the whole thing however. If cotton, which has been treated with caustic soda of 14 per cent or more, is washed free of caustic soda and dried at about 105°C., the amount of adsorption decreases below that of washed cotton which has been dried at room temperature, but it does not go back to the value given by the raw cotton. We hoped that this meant that a suitable washing and drying reversed the change in the space lattice. X-ray tests (3) showed that this was not the case, and that the change in the x-ray space lattice is irreversible so far. The reversible part of the adsorption is therefore due chiefly to what one may call a sintering effect.

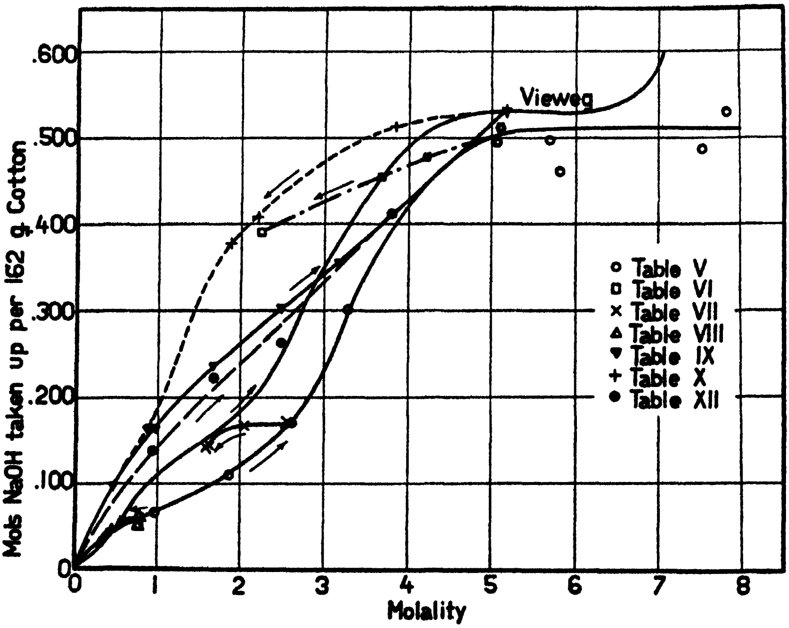

FIG. 5. SODIUM HYDROXIDE TAKEN UP BY CHANGE-IN-TITER METHOD

The general results of this paper are as follows:

1. The true amounts of adsorption of sodium hydroxide and water by

cotton can be ascertained by centrifuging the wet cotton and determining the point at which all the mother liquor has been driven off.

2. The Vieweg change-in-titer method measures only the caustic soda taken up in excess of the adsorbed solution and is consequently grossly inaccurate for this system.

3. The curve for the true adsorption of caustic soda by cellulose is a smooth curve, indicating that caustic soda is adsorbed by cellulose. There is no evidence of the existence in mass of any stoichiometric compound between sodium hydroxide and cellulose over the range up to 20 per cent caustic soda.

4. The curves for the apparent adsorption of caustic soda by cellulose (change-in-titer method) obtained by the German chemists would not justify the assumption of stoichiometric compounds, even if the data were true adsorption values, which they are not.

5. The apparent adsorption of caustic soda by cotton is a partially irreversible process except perhaps for dilute solutions of caustic soda.

6. The partial irreversibility is due to a change in space lattice, which is irreversible so far as the present facts go, and to a swelling which can be reversed more or less completely by heating at about 105°C.

7. The method herein developed for determining the true adsorptions of sodium hydroxide and water by cotton is a general method and can be applied to many other systems.

8. No experiments have yet been made on precipitated cellulose to determine the effect, if any, of the fibrous form of the cotton.

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THE WETTING CHARACTERISTICS OF GALENA

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Recent work has shown that the free surface energy of a solid, hence its wetting characteristics, may be altered much more easily than had previously been supposed. In view of this fact, it is apparent that the pretreatment of a solid surface must be carefully controlled if significant values of its wetting properties are to be obtained. It seems probable that failure to consider carefully the exact surface condition of the solid accounts for the fact that existing data on wetting properties of solids show such an outstanding lack of agreement.

In recent years much work has been done in an effort to determine the wetting characteristics of galena, such information being highly desirable in connection with the ore flotation industry. The angle of contact of water on galena has been used as a measure of its wetting characteristics and there has been a surprising lack of agreement in the data which have been obtained. Sulman (11) found the advancing water–air angle for one sample of galena to be 73°, and for another 70°, the respective receding angles being 35° and 41.6°. Langmuir (9) obtained an angle of 86°, while Coghill and Anderson (5) found angles from 45° to 60°. These angles were apparently advancing angles. In none of these cases are we certain as to the exact condition of the surfaces. Wark and Cox (12) found an "equilibrium" angle of zero degrees for water upon a galena plate cleaved under water, the angle they measured being in reality a receding angle. They found that a finite angle was formed if the galena was cleaved in air and assumed that the difference was caused by contamination. Rehbinder, Lipetz, Remskaja, and Taubman (10) obtained a 47° advancing and a zero receding angle for water upon freshly cleaved galena.

In view of the lack of agreement in the literature concerning galena, we felt that a study of this solid should yield information of value. Our primary object was to determine the wetting characteristics of the galena surface by measurement of contact angles and to study the factors which might influence such measurements. This objective led to the investigation of the following factors:

1. Different methods for measuring contact angles.
2. The phenomenon of "hysteresis" of the angle of contact, i.e., the relation of the advancing to the receding angles.

3. The effect of the pretreatment of the solid surface upon the angle of contact.

SIGNIFICANCE OF CONTACT ANGLES

The degree of wetting or adhesion tension of a liquid against a solid has been defined as that change in free surface energy which occurs when a solid–air surface is replaced by a solid–liquid interface. The adhesion tension is related to the contact angle as follows:

$A_{13} = S_3 \cos \theta_{13}$ (8), where A_{13} represents the adhesion tension, liquid against solid, S_3 the surface tension of the liquid, and $\cos \theta_{13}$ the cosine of the contact angle between liquid and solid in air.

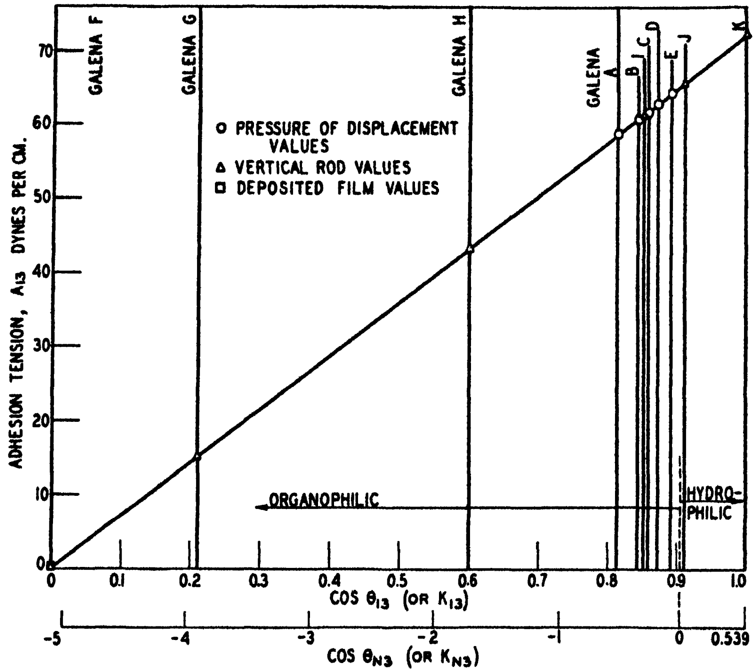

FIG. 1

It has been found from numerous studies in our laboratory that solids on which water gives a contact angle greater than approximately 25° ($\cos \theta_{13} = 0.90$) are organophilic in nature, i.e., they are preferentially wetted by organic liquids, while those giving an angle less than 25° are hydrophilic (1) and are preferentially wetted by water. The change in wetting properties progresses with change in contact angle (or $\cos \theta_{13}$).

In the present paper we shall express the wetting characteristics of the different solids in terms of the cosine of the solid–water–air contact angle, $\cos \theta_{13}$ (or K_{13})—and shall consider that the solids are organophilic when

$\cos \theta_{13} < 0.90$ and that they are hydrophilic when $\cos \theta_{13} > 0.90$. Straight line graphs, of slope S_3, may be made by plotting A_{13} against $\cos \theta_{13}$ (see figure 1). The position of a solid on the horizontal, $\cos \theta_{13}$, axis will show the relative degree of organophilic or hydrophilic nature of the solid.

QUALITATIVE WETTING TESTS

Preliminary studies on the wetting characteristics of galena powder yielded some rather surprising results. It was found that if the powdered material was first wetted with water, an organic liquid could not readily be stirred into the resulting paste, while if it was first wetted with an organic liquid, water could not readily be stirred into it. When the powder was packed into a U-tube, or a displacement pressure cell, half of the powder being wetted with the organic liquid and the remainder with water, no displacement of one liquid by the other occurred. To cause movement of the interface in either direction it was necessary to apply an external force. Once this force was removed, the line of contact of the interface with the solid appeared to remain fixed.

When these qualitative tests were repeated, using carbon or silica, entirely different results were obtained; the organic liquid would completely displace water from the carbon, and water would completely displace the organic liquid from the silica. In contrast to the behavior of these two solids, galena appeared to be preferentially wetted by either liquid, depending upon which was first present. Thus, if the galena was first wetted with water it behaved similarly to the hydrophilic silica, whereas if it was first wetted with the organic liquid it behaved as the organophilic carbon. It should be stressed that this wetting produced no permanent change of the surface. If the powder was dried after being wetted with water or with a volatile organic liquid, it behaved exactly as the freshly prepared material.

MATERIALS

Liquids

Liquids used in this investigation were water, benzene, *n*-butyl acetate, and α-bromonaphthalene. All were carefully purified, and their densities, surface tensions, and interfacial tensions (against water) agreed, within the limits of experimental error, with the generally accepted values. The following surface tension and interfacial tension values respectively (for 25°C.) were used in our calculations: water, 72.08; benzene, 28.22 and 34.00; *n*-butyl acetate, 24.06 and 13.17; α-bromonaphthalene, 44.00 and 41.57.

Solids

Galena in the form of powder, plates, rods, and films was used. In the measurement of contact angles by the pressure of displacement method, finely ground galena was used, which had been graded through sieves between 250 and 300 mesh. The graded galena was first shaken with acetone to remove possible traces of oils, etc., dried, then thoroughly mixed in a rotating cylinder.

TABLE 1

Contact angle data for galena by the displacement pressure method (advancing air–water–solid contact angles)

t = 25°C. ± 0.10°; r (pore radius) = 8.18 × 10^{-4} cm.

SOLID	DISPLACEMENT PRESSURE	θ_{13} (ADVANCING)	cos θ_{13}	A_{13}
	grams per sq. cm			
Galena A	146	35.4°	0.815	58.7
Galena B	151	32.5°	0.843	60.7
Galena C	154	31.1°	0.856	61.7
Galena D	156	29.5°	0.870	62.7
Galena E	160	27.1°	0.891	64.2

The receding contact angles for the different samples of galena were all zero angles.

TABLE 2

Interfacial contact angle data for untreated galena by the pressure of displacement method

t = 25°C. ± 0.10°; galena A (r = 8.18 × 10^{-4} cm.)

LIQUID	DISPLACEMENT PRESSURE	S_{n2} cos θ_{n3}	θ_{n3}	cos θ_{n3} (K_{n3})	A_{1n}
Water advancing					
					dynes per cm.
n-Butyl acetate	−16.2	−6.52	119.7°	−0.495	65.2
Benzene	−41.9	−16.8	119.6°	−0.494	75.5
α-Bromonaphthalene	−51.0	−20.6	119.5°	−0.493	79.3
Average			119.6°	−0.494	
Water receding					
n-Butyl acetate	30.1	12.1	23.5°	0.917	
Benzene	75.5	30.3	27.0°	0.891	
Average			25.3°	0.904	

The following table shows the treatments to which the various samples of the graded galena powders were subjected:

Sample	*Treatment*
Galena A	No further treatment
Galena B	Heated in air for 2 hours at 180–190°C.
Galena C	Heated in air for 4 hours at 180–190°C.
Galena D	Heated in air for 8 hours at 180–190°C.
Galena E	Heated in air for 24 hours at 180–190°C.

TABLE 3

Interfacial contact angle data for galena A heated in air at 180–190°C. for different lengths of time; pressure of displacement method (water advancing)

$t = 25°C. \pm 0.10°$; $r = 8.18 \times 10^{-4}$ cm.

LIQUID	DISPLACEMENT PRESSURE	θ_{1n}	$S_{n3} \cos \theta_{n3}$	θ_{n3}	$\cos \theta_{n3}$ (K_{n3})	A_{1n}
Heated 2 hours = galena B						
						dynes per cm.
Benzene	−33.0	0°	−13.3	113.0°	−0.390	74.0
α-Bromonaphthalene	−42.2	0°	−16.9	114.0°	−0.407	77.6
Average				113.5°	−0.398	
Heated 4 hours = galena C						
Benzene	−24.2	0°	−9.71	106.6°	−0.286	71.4
α-Bromonaphthalene	−30.4	0°	−12.2	107.0°	−0.290	73.9
Average				106.8°	−0.288	
Heated 8 hours = galena D						
Benzene	−17.1	0°	−6.87	101.7°	−0.202	69.6
Heated 24 hours = galena E						
Benzene	−10.9	0°	−4.38	97.4°	−0.129	68.6

EXPERIMENTAL

In the course of this investigation four different methods for measuring the angle of contact were used, namely: (a) a pressure of displacement method; (b) a horizontal plate method; (c) a vertical rod method; and (d) a deposited film method. In the following section these four methods, together with the apparatus and its manipulation, will be discussed.

(a) *Pressure of displacement method for the measurement of contact angles*

The pressure of displacement method used was that described by Bartell and Walton (4). Both the advancing and receding contact angles were determined for the different galena–water–air systems and the different galena–water–organic liquid systems. The results obtained for the former systems are given in table 1, and for the latter systems in tables 2 and 3. The cosines of the different contact angle values galena–water–air (i.e., cos θ_{13} values) are plotted against adhesion tension values (A_{13}) in the wetting characteristics graph in figure 1, and the cosine of the interfacial contact angle values (i.e., cos θ_{n3} or K_{n3} values) are plotted against adhesion tension values in figure 2.[1]

The adhesion tension values, A_{1n}, for the organic liquids against the different galenas were calculated from the advancing galena–water–air

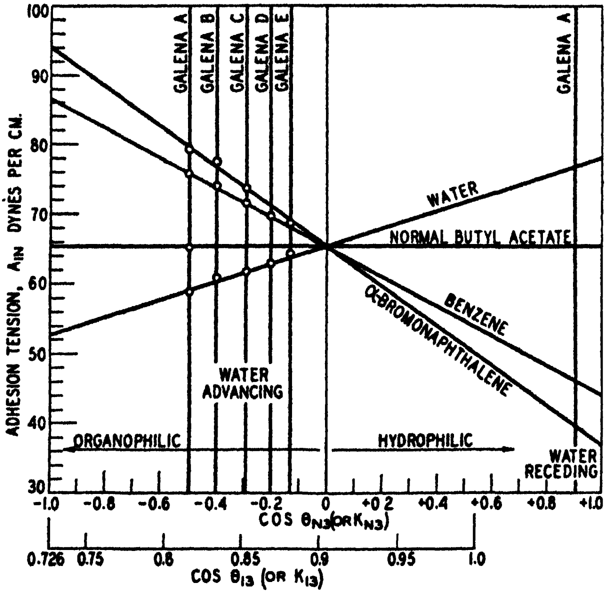

FIG. 2

and galena–water–organic liquid contact angle values from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (3). The results were found to be in agreement with the linear relationship noted for similar systems by Bartell and Bartell (1). The effect of the heat treatment was similar in nature to that observed by Bartell and Walton (4) for stibnite, the powder becoming less organophilic the longer the period of heating.

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[1] The adhesion tension versus cos θ_{n3} or K_{n3} values shown in figure 2 were plotted according to the relationship observed by Bartell and Bartell (1) and were determined by their empirical equations: $m_n = 12.8 - S_{n3}$ (where m_n is the slope of the organic liquid line and S_{n3} the interfacial tension water–organic liquid), and equation $A_{1n} = m_n K_{n3} + 65.2$ (where A_{1n} = adhesion tension of the organic liquid against the solid of corresponding K_{n3} value). The position of each solid on the horizontal axis (i.e., the wetting characteristics value) was determined from the galena–water–organic liquid systems, being the average of the cosines of the interfacial contact angles.

It will be noted that according to the advancing angles all the samples are organophilic in nature, while according to their receding angles they are all hydrophilic. It will be noted also that all the advancing interfacial angles for a given sample of galena give the same value. Likewise all the receding values are practically the same.

From the above discussion it is evident that galena, from the standpoint of its wetting characteristics, acts as two different solids depending upon whether or not it is wetted with water. Thus the pressure of displacement method quantitatively confirms the qualitative tests, previously cited, regarding the wetting characteristics of galena.

The values obtained for galena by the pressure of displacement method were duplicable to within ±2 per cent. This deviation was slightly greater than that which has previously been found for the method (±1 per cent), the cause lying in the nature of the solid.

If we have a water–organic liquid interface in a membrane composed of galena powder, neither liquid will displace the other until a definite pressure is applied, the pressure necessary to cause the water to displace the organic liquid corresponding to the advancing contact angle value, and that necessary to cause the organic liquid to displace the water corresponding to the receding contact angle value. The system is apparently stable anywhere between these two limits. If, at any time in the course of the determination, the pressure falls to a value between those corresponding to the advancing and the receding contact angles, the pressure will remain at this value, there being no tendency for the interface to move and build up the pressure.

Since there was reason to believe that the surface of the original finely divided particles of powder might have been altered during their preparation (i.e., oxidized during the processes of grinding, sieving, and mixing), it was decided to attempt to obtain a fresh non-worked and non-oxidized surface. Crystals of galena were therefore cleaved, and measurements were made of angles formed by drops of water upon the cleaved surface. This method will be referred to as the horizontal plate method.

(b) *Horizontal plate method for the measurement of angles of contact*

This method consisted essentially in measuring the dimensions of small drops of a liquid resting upon a plane solid surface. Since small drops are approximately segments of spheres, the angle of contact may be calculated from their height and diameter, using the following equation:

$$\tan\frac{\theta}{2} = \frac{h}{r}$$

where h is the height of the drop, and r is the radius of the drop.

A freshly cleaved surface of the solid was placed in a small covered absorption cell having plane glass sides, the atmosphere within the cell having previously been saturated with the liquid the contact angle of which was to be measured. A small drop of the liquid was then introduced upon the surface of the solid. The height and diameter of this drop were measured by means of a cathetometer. The direction of motion of the liquid (i.e., advancing or receding) was controlled by adding or withdrawing liquid from the drop. One set of representative results is given in table 4.

Each of the determinations gave a zero receding water–air angle, but the finite advancing values were very erratic and varied by as much as 30°. The cause for this variation, we believe, lies in the methods used for introducing the liquid drop onto the solid surface. Several different methods were tried, the drop being added by means of a glass rod, a small glass pipet, and from a paraffin-coated rod, but none proved entirely satisfactory. It is almost impossible to place a liquid drop upon the solid by means of a pipet or rod, and remove the pipet or rod without causing some vibration during the process. This vibration will cause the drop momentarily to flatten, the result being that the angle will exceed the advancing value and spreading will occur. Since this system is apparently stable with contact angles anywhere between the characteristic advancing and receding values, it will remain at an intermediate value. Some of the liquid is very apt to adhere to the rod or pipet upon its removal, and this also may cause the angle to be lower than the true advancing value. In spite of the common usage of this method, the importance of these sources of error has not been sufficiently stressed and different investigators have failed to take them into consideration, the result being that their advancing contact angle values have been too low.

TABLE 4

Contact angle data for water upon freshly cleaved galena surfaces by the horizontal plate method

$t = 25°C. \pm 1.0°$

EXPERIMENT	θ_{13} (ADVANCING)	θ_{13} (RECEDING)
1	76°	0°
2	80°	0°
3	90°	0°
4	57°	0°
5	67°	0°

The results of these measurements led us to believe that were it possible to cause the line of contact to advance slowly or recede slowly, one might obtain definite and characteristic values. Accordingly, the vertical rod method (2) was next tried.

(c) *Vertical rod method for the measurement of angles of contact*

A small freshly cleaved rod of the solid (approximately 3.0 × 3.0 × 12.0 mm.) was held in a vertical position in such a manner that it could be slowly raised or lowered. The rod was carefully adjusted to such a position that two of its sides were parallel to the plane of light entering the camera. The rod was then slowly lowered until it extended through the liquid surface, the liquid being contained in a small glass absorption cell having parallel plane sides, and the line of contact of the liquid surface with that of the rod was photographed. The advancing liquid–air contact angle was measured from the resulting photographic plate. The rod was then slowly raised until the liquid gradually receded from its surface, and the receding liquid–air contact angle thus formed was photographed.

TABLE 5

Contact angle data for galena by the vertical rod method; alteration of surfaces by heating in air

$t = 25°C. \pm 1.0°$; time of heating = 1 hour

SAMPLE	TEMPERATURE OF HEATING	θ_{13}	$\cos\theta_{13}$	K_{n3} (CALCULATED)	A_{13}
	degrees C.				*dynes per cm.*
Galena F (untreated)	25	90°	0.0	−5.09	0
Galena G	100	78°	0.21	−3.9	15.1
Galena H	200	53°	0.60	−1.7	43.4
Galena I	300	32°	0.85	−0.33	61.3
Galena J	400	24°	0.91	0.03	65.6
Galena K	500	0°	1.0	>0.54	>72.1

The value of the advancing water–air contact angle obtained with this method was 90° ($\cos\theta_{13} = 0$), and the value of the receding angle was zero ($\cos\theta_{13} = 1$). Since the advancing water–air angle obtained by this method was much larger than that obtained by the displacement pressure method, tests were carried out on cleaved rods which had been heated at given temperatures for definite periods of time. The results obtained with such rods are given in table 5.

The data obtained have been placed upon the graph in figure 1 (according to Bartell and Bartell (1)). It will be noted that the wetting characteristics were greatly altered by the heat treatment, passing from the strongly organophilic condition ($\cos\theta_{13} = 0$) to progressively lesser organophilic conditions and finally to what appears to be a definitely hydrophilic condition.

The contact angles measured upon freshly cleaved galena surfaces by the vertical rod method were duplicable to within ±3°. The advancing water–air angles of contact upon the heat-treated galena rods were considerably less duplicable, the cause apparently lying in the uneven alteration of the surface of the rods.

The results with the vertical rod confirmed our earlier views that failure to obtain definite and reproducible values with the horizontal plate method was caused by our inability to alter gradually the solid–liquid–air point of contact. Better control of the drop on the plate could be obtained by bringing the liquid through a hole in the plate, causing the drop to expand or contract. Since the drilling of galena plates offered some difficulty, and inasmuch as it is rather difficult to obtain perfectly smooth and plane surfaces by the cleavage of crystals, a method was devised which enabled us to accomplish the objectives mentioned above. This method will be referred to as the deposited film method.

(*d*) *Deposited film method for the measurement of angles of contact*

Numerous investigators have obtained mirror surfaces of various substances by slowly distilling the material in a high vacuum and condensing it upon the object it is desired to coat. We have employed this method in the preparation of surfaces for contact angle measurements.

In recent years considerable work has been carried out on the structure of deposited films. Finch and Quarrell (7) found that very thin films showed a distortion of crystal units, these tending to fit the lattice of the material of the base upon which they were deposited. They found the crystal structure of thicker films to be normal, the surface having a random orientation unless heated. In such a case orientation occurred. Dixit (6) found the orientation to be independent of the nature of the base, provided its surface was smooth and amorphous. This work appears to show that freshly deposited surfaces should be ideal for our purpose, provided the film is deposited upon a smooth and amorphous base.

The substance to be studied was deposited upon a polished glass surface having a small hole through the center (i.e., a tip, see figure 3). A drop of the liquid, the contact angle of which was to be measured against this solid, was introduced onto the surface by forcing the liquid up through the hole, and the angle of contact formed was then photographed. By proper manipulation of the apparatus both advancing and receding angles could be measured.

The method used in measuring the angles formed upon these deposited surfaces was a modified horizontal plate method. The arrangement for running the liquid out onto the plate permitted accurate control of the movement of the drop. Moreover, the system was comparatively free from vibration. In order to insure true advancing and receding values, the angle was photographed while the liquid was moving very slowly. The surface of the solid must not be in an inverted position if materials giving an angle greater than 90° are used, as in such a case the drop advances to approximately 90°, elongates, and then falls off.

Data for advancing and receding water–air angles upon these different deposited films are given in table 6. It will be observed that the water–air contact angles formed upon galena surfaces were the same as those which were found by the rod method, using freshly cleaved, unheated galena.

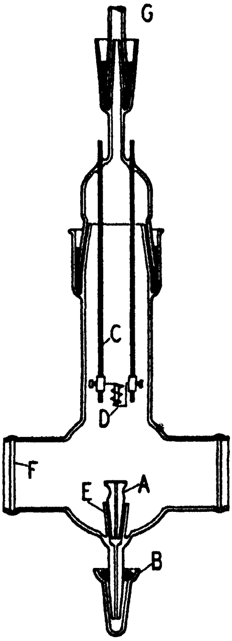

FIG. 3. APPARATUS FOR THE MEASUREMENT OF ANGLES OF CONTACT IN AN INERT ATMOSPHERE BY THE DEPOSITED FILM METHOD

A, tip; B, cap and seal; C, tungsten leads; D, heating coil; E, tip support; F, plane glass windows; G, vacuum outlet.

TABLE 6

Contact angle values of water upon deposited films

$t = 25°C. \pm 1.0°$

MATERIAL	θ_{13} (ADVANCING)	θ_{13} (RECEDING)
Lead sulfide	90°	0°
Arsenious sulfide	97°	0°
Bismuth	110°	0°
Sulfur	98°	66°
Biphenyl	107°	35°
Naphthalene	103°	35°

The angles of contact measured by this method were duplicable to within ±3°. The method has a very wide range of applicability. Other investigators have used the vacuum sublimation process for the preparation of mirror surfaces of practically all of the metals, a large number of salts, and several oxides. Our own work has indicated that many sulfides and organic materials would give good mirror films. Results obtained for some of these systems are given in table 6. The method should also be applicable to materials which are very readily oxidized by exposure to the atmosphere, as slight modifications in the design of the apparatus would allow the determination of contact angles upon these deposited films to be carried out in an inert atmosphere, or even *in vacuo* (see figure 3). Work is being extended along this line.

We believe that the process for preparing fresh mirror surfaces of various solids by sublimation of the material *in vacuo* could be advantageously used in the preparation of surfaces for the measurement of contact angles by other methods.

DISCUSSION OF METHODS AND RESULTS

A study of the methods used in this investigation for the measurement of contact angles reveals that each of the methods may be satisfactory for certain systems.

The pressure of displacement method gives duplicable and apparently significant results. It is the only method suitable for use with powdered materials. In case the surface properties of a solid become altered in the process of pulverization (which may sometimes be the case), this method obviously would not give values characteristic of an uncontaminated surface of the pure substance.

The horizontal plate method as generally employed is suitable for use with certain substances, but not for substances which give dual contact angles (advancing and receding angles), each of which is apparently stable, unless some means is employed to control very accurately the spreading of the drop.

The vertical rod method appears to give reliable results with those substances which will give clean smooth surfaces of proper shape.

The deposited film method is primarily suited for the determination of angles of contact upon pure materials, films of which can be formed by sublimation. This method offers greatest possibilities in fundamental studies of pure and uncontaminated surfaces.

Results obtained with the vertical rod method and with the deposited film method indicated that with a strictly clean galena surface the galena–water–air advancing contact angle is one of 90°, and that the receding angle is zero.

Results obtained using powdered galena and the pressure of displacement method indicated that the surface of the powdered galena used was less organophilic than was that of the freshly cleaved or freshly sublimed galena used in the vertical rod method and in the deposited film method. By heat treatment the galena used in the vertical rod method could be caused to approach in surface properties the powdered galena. In these cases it is believed the change in surface properties was caused by oxidation.

A study of all the results obtained with galena indicates that this solid has surface properties quite different from other solids previously studied by us (as carbon and silica), in that it gives widely different and apparently stable advancing and receding contact angles and in so doing appears to function either as an organophilic or as a hydrophilic solid depending upon whether it is first wetted by an organic liquid or by water. From data given in table 6, obtained with the film method, it appears probable that other substances will be found to possess properties similar to those exhibited by galena.

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X-RAY STUDIES ON THE HYDROUS OXIDES. VII

Ferric Oxide

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THE BROWN GEL

The interaction of solutions of ferric salts and soluble bases gives a highly gelatinous precipitate of hydrous ferric oxide, frequently misnamed ferric hydroxide. The composition and other properties of this brown gel depend upon the conditions of formation and the age of the sample. Heating under water (1, 4, 5, 8, 12) or dilute salt solutions (2) for a long time, or aging at room temperature (14) for a much longer time, gives an almost anhydrous, more or less brick-red product. X-ray analysis by Böhm (2) showed that boiling in the presence of water, potassium chloride, or ammonium chloride solutions gives α-Fe_2O_3, whereas aging at 150°C. in the presence of 2 *M* potassium hydroxide gives α-$Fe_2O_3 \cdot H_2O$. Katsuria and Watanabe (9) obtained the α-Fe_2O_3 x-ray pattern from a gel heated to 150°C. in an autoclave. Nichols, Kraemer, and Bailey (11) obtained the α-Fe_2O_3 pattern for the coagula from aged sols.

Although all the evidence points to the aged gel being α-Fe_2O_3, it is generally agreed that the x-ray diffraction pattern of the freshly precipitated oxide shows no lines or bands (2,3,6,7,15). The results of a systematic study of the transformation from the brown gel to α-Fe_2O_3 are given in the following section.

Aging under water and ferric chloride solutions

The brown gel was precipitated at about 20°C. by the addition of 300 cc. of 15 *M* ammonium hydroxide to 1 liter of 0.2 *M* ferric chloride solution. The precipitate was washed with dilute ammonia by the use of the centrifuge until free of chloride, and finally with water until only a trace of ammonia remained. Samples of the washed brown gel were aged as indicated in table 1. X-ray analysis of the products shows that, although no lines or bands can be detected in the original gel, the lattice of α-Fe_2O_3 appears gradually upon aging in the cold, and more rapidly at 100°C. In figure 1 are given densitometer curves (10) of the x-ray negatives for the products aged at 100°C. These show clearly the progress of the transformation from the brown gel to α-Fe_2O_3.

Aging in the presence of electrolytes

Since the results in table 1 show that the presence of ferric chloride delays the transformation from the brown gel to α-Fe_2O_3, a systematic study of the effect of added electrolytes was undertaken. The brown gel was precipitated at 32°C., as described above, and all washings were carried out by decantation without using the centrifuge. The washing was facilitated by this procedure, since the matting of the precipitate was avoided. Samples were aged in the presence of ammonium hydroxide, ammonium chloride, ferric chloride, and hydrochloric acid. Ten additional samples were aged under pure water as a control experiment. The results are summarized in table 2. It is apparent that added electrolytes retard or prevent the transformation from the brown gel to α-Fe_2O_3. The higher temperature of precipitation of 32°C., as compared with 20°C. in the preceding experiments, allowed the transformation to proceed more rapidly. This conclusion is further substantiated by the observation that a separate sample, precipitated at 100°C. and cooled rapidly to room temperature, gave a good pattern of α-Fe_2O_3 without further aging.

TABLE 1

Aging of $Fe_2O_3 \cdot xH_2O$ *in the presence of water and ferric chloride solutions*

AGING MEDIUM	TEMPERATURE	TIME OF AGING	RESULTS OBTAINED BY X-RAY ANALYSIS	COLOR
Water	Room temperature	0	No lines or bands visible	Brown
		8 days	No lines or bands visible	Brown
		3 months	No lines or bands visible	Brown
		5 months	One or two weak broad bands	Brown
		6 months	Weak α-Fe_2O_3 pattern	Brown
		1 year	Good α-Fe_2O_3 pattern	Brick-red
		2 years	Good α-Fe_2O_3 pattern	Brick-red
Water	100°C.	0	No lines or bands visible	Brown
		1 hour	α-Fe_2O_3 pattern, broad bands	Brown
		2–16 hours	α-Fe_2O_3 pattern, broad lines	Brick-red
		19 hours	α-Fe_2O_3 pattern, sharp lines	Brick-red
Ferric chloride solution	100°C.	0	No lines or bands visible	Brown
		1 hour	α-Fe_2O_3 pattern, few broad bands	Brown
		6 hours	α-Fe_2O_3 pattern, few broad bands	Brown
		24–36 hours	α-Fe_2O_3 pattern, broad lines	Some brick-red

THIESSEN AND KÖPPEN'S "HYDRATES"

Thiessen and Köppen (17) have recently reported the preparation of a series of ferric oxide hydrates by the slow hydrolysis of ferric ethylate.

From breaks in dehydration isotherms they deduce the formation of $Fe_2O_3 \cdot nH_2O$ where $n = 4, 7/2, 3, 5/2, 2, 3/2, 1, 1/2$, and probably 5 and 9/2.

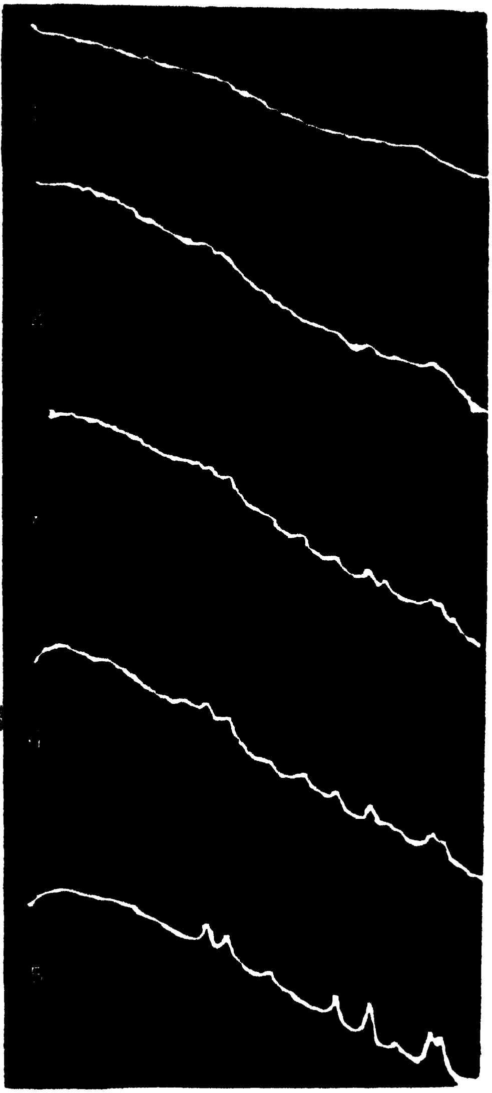

FIG. 1. DENSITOMETER CURVES FOR $Fe_2O_3 \cdot xH_2O$ AGED UNDER WATER AT 100°C.
Time of aging in hours: (1) 0; (2) 1; (3) 2; (4) 4; (5) 19

The existence of such a series of oxide hydrates is so unusual that it seemed advisable to confirm or disprove Thiessen and Köppen's experiments.

TABLE 2

Aging of $Fe_2O_3 \cdot xH_2O$ *at room temperature*

ELECTROLYTE ADDED	CONCENTRATION	COLOR OF PRECIPITATE AFTER				
		10 minutes	6 hours	40 days	125 days	10 months
	N					
NH_4OH	15	Brown	Brown	Brown	Brown	Brown
	11.3	Brown	Brown	Brown	Brown	Trace brick-red
	7.5	Brown	Brown	Brown	Brown	Trace brick-red
	3.8	Brown	Brown	Brown	Trace brick-red	Trace brick-red
	1.5	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.75	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.50	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.25	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.05	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
NH_4Cl	5.0	Brown	Brown	Brown	Brown	Brown
	3.75	Brown	Brown	Brown	Brown	Brown
	2.5	Brown	Brown	Brown	Brown	Brown
	1.25	Brown	Brown	Brown	Brown	Brown
	0.5	Brown	Brown	Brown	Brown	Brown
	0.25	Brown	Brown	Brown	Brown	Brown
	0.03	Brown	Brown	Brown	Brown	Trace brick-red
$FeCl_3$	0.5	Brown	Brown	Brown*	Brown*	Brown*
	0.25	Brown	Brown	Brown*	Brown*	Brown*
	0.10	Brown	Brown	Brown*	Brown*	Brown*
	0.01	Brown	Brown	Brown*	Brown*	Brown*
HCl	0.10	Brown	Brown	Brown	Red sol	Red sol
	0.01	Brown	Brown	Brown	Brown	Red sol
H_2O only		Brown	Brown	Brick-red	Brick-red	Brick-red

* Deposits a yellow sediment (probably β-$Fe_2O_3 \cdot H_2O$).

Preparation of ferric ethylate

Samples of ferric ethylate were prepared by the interaction of solutions of anhydrous ferric chloride and sodium ethylate in absolute alcohol. In the first experiments the alcohol was dehydrated with metallic calcium, as was done by Thiessen and Köppen. At all times the apparatus and solutions were protected from the action of moisture in the air by the use of large drying towers containing calcium chloride and phosphorus pentoxide. A solution 15 millimolar with respect to ferric oxide in absolute alcohol was prepared from the ferric ethylate. Moisture from the air was allowed to diffuse into the solution, causing a slow hydrolysis which was complete at the end of three or four weeks, the exact time depending upon the atmospheric conditions prevailing during the hydrolysis period. Several samples prepared in this way were separated from the supernatant liquid and washed thoroughly, using the centrifuge, with alcohol alone or first with alcohol and then with water. The samples washed with alcohol alone contained considerable adsorbed alcohol, which was largely removed by washing with water. The following analytical results are typical: Sample washed with alcohol alone: Fe_2O_3 = 68.03 per cent; H_2O = 24.53 per cent; C_2H_5OH = 7.54 per cent. Sample washed with alcohol and with water: Fe_2O_3 = 64.14 per cent; H_2O = 34.85 per cent; C_2H_5OH = 1.01 per cent. The amount of adsorbed alcohol was determined by a combustion method. The samples actually used in dehydration experiments were always washed with water to remove excess alcohol. Since only 1 per cent of alcohol remained in the samples washed in this way, its presence may be neglected in the dehydration experiments described in the next section.

In a second series of experiments an improved method of drying the alcohol was adopted (16). "Absolute alcohol" was further dried with excess metallic calcium and distilled directly into a carefully dried flask containing metallic sodium and ethyl oxalate. Traces of water in the alcohol react with the sodium ethylate to give alcohol and sodium hydroxide. The reaction is shifted in the desired direction by allowing the sodium hydroxide to hydrolyze the ethyl oxalate, giving alcohol and sodium oxalate. The resulting highly anhydrous alcohol was distilled directly into the reaction vessels containing anhydrous ferric chloride and metallic sodium. The solutions of ferric chloride and sodium ethylate were mixed, giving ferric ethylate. The entire apparatus and solutions were protected from the action of moisture in the air by calcium chloride and phosphorus pentoxide towers. The slow hydrolysis of this sample of ferric ethylate was carried out in warmer weather than the first; hence the resulting ferric oxide gel contained less adsorbed water than the first preparation.

Dehydration isotherms

The samples of hydrous ferric oxide prepared as described above were dehydrated isothermally in an apparatus shown in figure 2, which needs no further description. The general method of procedure consists in pumping off a definite amount of water and measuring the vapor pressure of the resulting product at constant temperature by means of a manometer filled with "vacuum pump oil" of known density. In the case of the sample made from the alcohol dried with metallic calcium only, the weighed sample was sealed into the weighed tube, A, and changes in composition were followed by closing the stopcock and reweighing the tube with contents. Typical isotherms are given in figure 3.

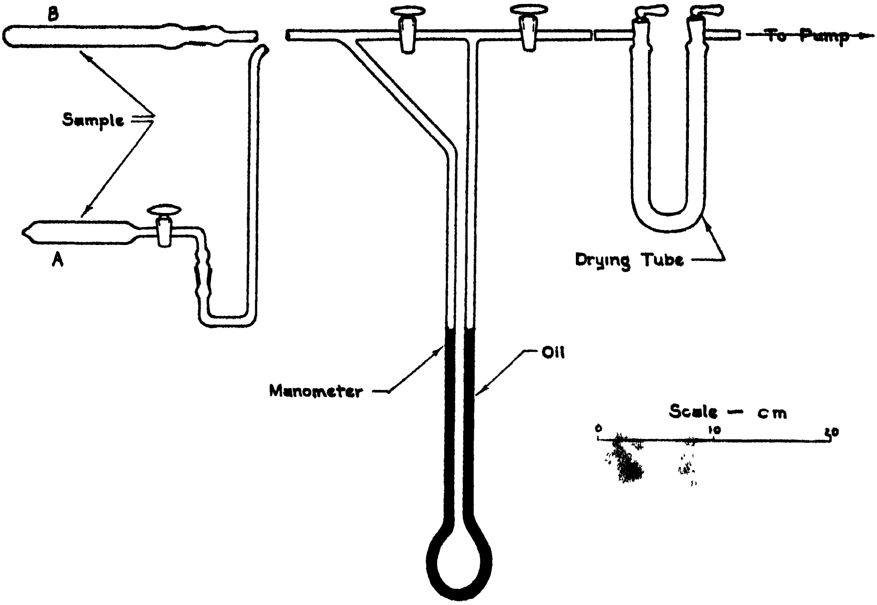

FIG. 2. APPARATUS FOR ISOTHERMAL DEHYDRATION

An improvement was made in the apparatus used in the isothermal dehydration of the samples made from the drier alcohol. Tube B was substituted for tube A, and changes in composition were followed by collecting the water vapor in a drying tube filled with magnesium perchlorate trihydrate. Otherwise the apparatus was unchanged. Typical isotherms for this sample are given in figure 4. The equilibrium pressure at a given temperature and composition is established in half an hour or less. The pressure was read only after it had remained constant for half an hour. It is obvious that the isotherms contain no breaks which would suggest the existence of hydrates in the gel. We have no explanation to offer for the series of breaks at just the right place in the isotherms of Thiessen and Köppen. Since these observers made no statement to the contrary, it is probable that they neglected to remove the alcohol from their samples before dehydration. This might account for one point of inflection in the curve, but it would come at a point corresponding to a hydrate only by accident.

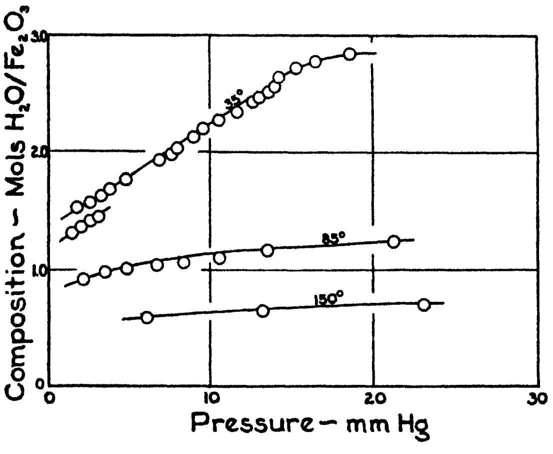

Fig. 3. Dehydration Isotherm for $Fe_2O_3 \cdot xH_2O$

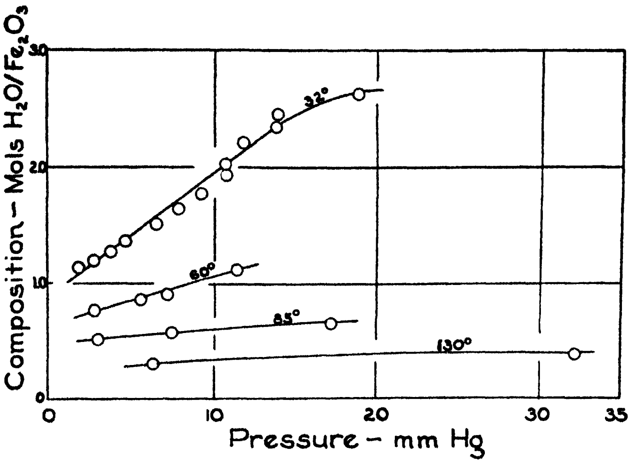

Fig. 4. Dehydration Isotherm for $Fe_2O_3 \cdot xH_2O$

X-ray analysis

The freshly precipitated samples, either unwashed, washed with alcohol, or washed with both alcohol and water, gave x-ray patterns showing no lines or bands. A sample washed with water and heated to about 185°C. gave a weak pattern corresponding to α-Fe_2O_3. The broad bands indicated extremely small particle size.

HYDROLYSIS OF FERRIC SALTS

A. Ferric sulfate

The system Fe_2O_3–SO_3–H_2O has been examined in detail by Posnjak and Merwin (13, 18), using phase rule methods. These investigators have proven that α-$Fe_2O_3 \cdot H_2O$ may be prepared by the hydrolysis of ferric sulfate at low concentrations and at temperatures below 130°C. More concentrated solutions give a basic salt of composition $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The following experiments are in agreement with these observations. Solutions of ferric sulfate were prepared as indicated in table 3. The solutions were heated to the boiling point on a hot plate, using reflux condensers to prevent loss of water vapor. The more dilute solutions gave α-$Fe_2O_3 \cdot H_2O$, while the yellow precipitate obtained in the more concentrated solutions gave the same x-radiogram as the basic salt reported by Posnjak and Merwin.

TABLE 3

Hydrolysis of ferric sulfate solutions

CONCENTRATION	COLOR OF PRECIPITATE	SOLID PHASE IDENTIFIED BY X-RAY ANALYSIS
M		
1.00	Yellow	Mostly basic sulfate
0.50	Yellow	Mostly basic sulfate
0.25	Yellow	Mostly basic sulfate
0.10	Yellow	Mostly basic sulfate
0.05	Yellow	Mostly basic sulfate
0.01	Yellow	Mostly α-$Fe_2O_3 \cdot H_2O$

B. Ferric nitrate

A solution containing 25 g. of ferric nitrate hexahydrate per liter was heated slowly to 100°C. on a hot plate; a yellow precipitate was obtained which gave the x-ray pattern for α-$Fe_2O_3 \cdot H_2O$. A 0.1 *N* solution was allowed to stand at room temperature for about seven months. This was likewise identified as α-$Fe_2O_3 \cdot H_2O$. More concentrated solutions were not examined. Simon and Schmidt (15) dialyzed a ferric nitrate solution and examined the precipitate from the resulting sol by x-ray diffraction methods. The pattern was reported as being different from α-Fe_2O_3; it was probably that for the α-monohydrate.

C. Ferric bromide and oxalate

Hydrolysis of ferric bromide and ferric oxalate gives a yellow precipitate which was proven by x-ray analysis to be α-$Fe_2O_3 \cdot H_2O$.

D. Ferric chloride

Slow hydrolysis of ferric chloride solutions, either dilute or concentrated, always gives a third polymorph of ferric oxide monohydrate, which has been designated elsewhere (20) as β-$Fe_2O_3 \cdot H_2O$.

E. Ferric acetate

Fifteen years ago one of us (19) found that boiling freshly prepared ferric acetate solutions gave a brick-red colloid or precipitate, whereas solutions aged for ten days or more before boiling gave a definitely yellow colloid or precipitate. At that time the available evidence pointed to the conclusion that this yellow product consisted of hydrous ferric oxide, differing from the red-brown and brick-red varieties only in particle size. These experiments have been repeated, and the yellow product has been identified as α-$Fe_2O_3 \cdot H_2O$ and the brick-red powder as α-Fe_2O_3.

TABLE 4

Slow hydrolysis of ferric salts

SALT USED	PRODUCT IDENTIFIED BY X-RAY ANALYSIS
Sulfate	α-$Fe_2O_3 \cdot H_2O$ or $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
Nitrate	α-$Fe_2O_3 \cdot H_2O$
Nitrate inoculated with a trace of β-$Fe_2O_3 \cdot H_2O$	α-$Fe_2O_3 \cdot H_2O$
Bromide	α-$Fe_2O_3 \cdot H_2O$
Oxalate	α-$Fe_2O_3 \cdot H_2O$
Chloride	β-$Fe_2O_3 \cdot H_2O$
Acetate	α-$Fe_2O_3 \cdot H_2O$

Rapid hydrolysis of ferric salts always yields α-Fe_2O_3, and slow hydrolysis, except in the case of the chloride, yields the α-monohydrate. Slow hydrolysis of the aged ferric acetate solutions in the cold gives nuclei of α-$Fe_2O_3 \cdot H_2O$, which determine the course of the reaction at higher temperatures.

Table 4 summarizes the results obtained by the slow hydrolysis of various ferric salts.

SUMMARY

The brown gel formed by the interaction of solutions of ferric salts and bases in the cold gives an x-radiogram showing no lines or bands. Aging under water of the oxide freshly precipitated in the cold for a few weeks or months at room temperature or a few hours near the boiling point brings about a transformation from the brown gel to brick-red α-Fe_2O_3. Excess electrolytes retard or prevent the transformation. X-ray examination of the products formed by systematic aging of the original gel indicates that the transformation consists in the growth of particles too finely divided to give a characteristic x-radiogram, to crystals of α-Fe_2O_3 large enough to give sharp diffraction lines. Gels thrown down near 100°C. give at once a weak x-radiogram of α-Fe_2O_3.

Dehydration isotherms of the ferric oxide gel formed by the slow hydrolysis of ferric ethylate show no breaks indicative of the existence of definite hydrates. This is contrary to the results of Thiessen and Köppen.

Rapid hydrolysis of ferric salts gives a brick-red precipitate identified by x-ray analysis as α-Fe_2O_3. Slow hydrolysis of ferric salts gives a yellow precipitate of hydrous α-$Fe_2O_3 \cdot H_2O$, except in the case of ferric chloride where β-$Fe_2O_3 \cdot H_2O$ is formed; ferric sulfate gives either α-$Fe_2O_3 \cdot H_2O$ or a definite basic sulfate, depending on the conditions.

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INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS. III

THE EFFECT OF ORGANIC STRUCTURE ON ADSORBABILITY[1]

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I. INTRODUCTION

Freundlich's observations (5) indicated a general relationship between adsorption and solubility and an apparent parallelism between surface tension lowering and extent of adsorption. Langmuir (20, 21) and Harkins (14 to 17) developed independently the idea of molecular orientation, first suggested by Hardy (11 to 13), and gave a definite picture of the arrangement of solute molecules at interfaces. Still later, in investigating the mechanism of bacterial action, Quastel and his coworkers came to the conclusion that there are certain active centers "characterized by the possession of particular groupings which are able to adsorb a particular type of structure. A relatively large number of substances can be adsorbed in this specific manner, but out of this number only a few can be activated to act as hydrogen donators" (36). This work demonstrates the importance of molecular structure in specific adsorption.

The literature, although it shows the importance of chemical configuration in adsorption phenomena, reveals no adequate study of several structurally related compounds on a single interface over any concentration range or any reasonable basis for comparison. This study was accordingly undertaken to compare the influence of certain groupings in typical organic acids on the adsorption of these compounds from aqueous solution within definite concentration ranges, using a single and comparable interface.

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[1] Paper No. 1291, Journal Series, Minnesota Agricultural Experiment Station. Greatly condensed from a thesis presented by E. R. Linner to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934. The detailed tabular experimental data are all included in a manuscript copy on file in the Library of the University of Minnesota. Photostatic copies of the detailed tables may be obtained approximately at cost from the University of Minnesota.

II. HISTORICAL

Surface tension lowering by solute and its relation to adsorbability

Following the establishment of the Freundlich (5) equation for adsorption, most studies dealt either with the relationships between solubility and adsorption or with the dependence of the phenomenon on surface tension lowering by the solute molecule. Freundlich has cited examples of a few substances which are strongly adsorbed from aqueous solution but which depress the surface tension of water only slightly, e.g., succinic acid and benzoic acid, together with some of the derivatives of the latter. Glucose, lactose, and cane sugar, although they raise the surface tension of water markedly, are all comparatively well adsorbed. Michaelis and Lachs (24) noted other exceptions, among them citric acid. King and Wampler (19) have shown that tartaric acid is negatively adsorbed at an aqueous interface, and that while fumaric acid has little effect on the surface tension of water, its isomer, maleic acid, lowers it slightly. Although the first three members of the series of dicarboxylic acids are positively adsorbed at an air–water interface, the effect is relatively small. However, all these compounds are adsorbed by charcoal and there is positive evidence that, to the limits of its solubility, fumaric acid is adsorbed to a greater extent than is maleic. Accordingly there can be no direct parallelism between surface tension lowering and adsorption.

Solubility and adsorption

Freundlich (5) pointed out that while there is a general relation between the solubility and the adsorbability of a solute there are still notable exceptions, e.g., benzenesulfonic acid and sulfanilic acid. The latter, though it is less soluble than the former, is less strongly adsorbed. The very soluble mellitic acid is strongly adsorbed. According to de Izaguirre (Freundlich (6) addenda, p. 817) in the case of maleic and fumaric acids and of citraconic and mesaconic acids, adsorption decreases with increasing solubility. Alekseevskii (1) confirmed this for fumaric and maleic acids, but found the opposite to be true for isobutyric and *n*-butyric acids. For six organic compounds, some of which are structurally related, Santa (40) showed that adsorption is greater the lower the solubility. Platonov, Borgman, and Salman (32, 33) and Roychoudhury (38) conclude that solubility is of only secondary importance.

With only few exceptions the conclusions summarized above are based on adsorption data obtained from series of experiments involving two or three different initial concentrations. However, some of these conclusions depend on ratios between "adsorbability" or the per cent adsorbed of two related compounds. It will be shown later that the numerical values for the $\frac{C_0 - C}{C_0} \times 100$ relationship can vary widely when calculated over a range of concentrations. In spite of this objection it is evident that there is no strict antibasis between adsorption and solubility.

Relation of polarity to adsorption

Aside from surface tension lowering of the solvent by the solute molecules and adsorbability, and the antibatic solubility–adsorbability relationship, many studies have dealt with the rôle played by the polarity of the molecule. Bartell and Miller (2) showed that the introduction of the hydroxyl group in an organic acid decreased adsorption on carbon to an extent depending on the nature of the acid. The introduction of the amino group produced a greater effect. Miller (25) states that charcoal plays the same rôle at a charcoal–solution interface that an organic liquid plays in an organic liquid–aqueous interface, and that the Langmuir-Harkins theory of polar groups applies to adsorption from solution by charcoal. Alekseevskii (1) ascribes the difference in adsorbability between *n*-butyric acid and isobutyric acid to the branched chain. Shilov and Nekrassov (41) conclude that normal compounds are more strongly adsorbed than are iso compounds and that the *trans* forms are more strongly adsorbed than are *cis* forms. Platonov, Borgman, and Salman (32, 33) conclude that structure is a most important factor in predicting the degree of adsorbability. Langmuir (21) pointed out that a stoichiometrical equation cannot be written for adsorption, because the configuration of the molecules adsorbed makes a difference in the areas taken up by them on the adsorbent.

In view of the demonstrated influence of molecular structure on adsorbability, it seems most unusual that this field of investigation has received such scant attention.

III. EXPERIMENTAL

The adsorbate

A series of thirty-one organic acids, differing in most cases regularly in chemical configuration, was employed throughout this study. All were of satisfactory purity. The list of the acids used is given in the first paragraph of the summary, and the individual acids are also indicated on the various graphs and tables.

The adsorbent

A large sample of decolorizing carbon, Norite, was secured, thoroughly sampled, and used throughout all studies. Thus variations of the interface were only those existing through the mass of adsorbent. The Norite contained 1.25 per cent ash (chiefly silica with traces of iron), which was found to have an equivalent of 1.5 cc. of 0.01 N acid. This percentage of extraneous material should invalidate in no way comparisons between structurally similar compounds. Miller (25) has pointed out that organic acids are strongly adsorbed on impure carbons and on such interfaces show the same selectivity as on ash-free carbon.

One gram of the adsorbent was used, except in those experiments involving caprylic acid. Caprylic acid is so slightly soluble that a weight of adsorbent greater than 0.1 g. tends to make the titre of the equilibrium concentration so low as to be of doubtful value. Fodor and Schönfeld (4) and Pavlov (31) have already shown variations in the amounts adsorbed with greatly diluted solutions and smaller amounts of carbon. The former authors point out that in the application of the Freundlich equation to their data, n varies notably with the amount of charcoal used, becoming less as the charcoal is increased. They report, however, that in the less dilute solutions n is independent of the amount of charcoal used. In the present study 1 g. of Norite and concentrations of reagents varying from 0.01 to 0.25 molar have been employed.

Experimental procedure

Where solubility permitted, stock solutions of the acids to be studied were made up to approximately 0.25 molar. With acids of limited solubility, saturated stock solutions were used. Aliquots of the stock solution were measured into Erlenmeyer flasks from a calibrated buret. Water was added to make the final volume 75 cc. One gram of Norite was then added. The flasks were closed with rubber stoppers and shaken with the adsorbent for a period of thirty minutes. They were then allowed to stand at room temperature for the same length of time. After this period they were filtered through #615 E. and D. filter paper into Erlenmeyer flasks. The filters were allowed to drain for fifteen minutes, after which the Erlenmeyers were removed and stoppered until titrations were made. To avoid errors due to adsorption by the filter paper, approximately the first 15 cc. of filtrate was discarded. A blank of 75 cc. of the stock solution without Norite was given the same treatment as each sample of the run.

In a few early experiments samples were allowed to stand in contact with the adsorbent overnight, but no essential differences were noted as a result of this longer period of contact. This is in accord with the observations of Freundlich (5), Dubinin (3), Lipatov (23), and Ruff (39).

The experiments were conducted at room temperature, which varied from 22°C. to 30°C. Freundlich (reference 6, pp. 174, 223–4) and Yajnik and Rana (42) found little change in adsorption over this temperature range.

Equilibrium concentrations were determined by titrating with standard solutions of sodium hydroxide, using phenolphthalein or thymol blue indicators. Equilibrium concentrations were calculated to moles per liter. The "adsorption in millimoles per gram" refers to the amount adsorbed by 1 g. of Norite from a volume of 75 cc. of solution.

Adsorption equations

From a consideration of the mosaic-like character of the solid surface, Langmuir (22) has made it clear that probably no single equation will express, in all cases, the relation between the equilibrium concentration and the quantity of adsorbed molecules. Many workers have stressed the complexity of the phenomena and the forces existing at surfaces. It is not the purpose of this paper to delve into any of these phases of the problem. The project at hand is one of showing the effect of molecular configuration of the adsorbate on adsorption. The difficulty of using isolated concentrations for comparison has been suggested above, and it will later be shown that in some cases the conclusions which authors have drawn can apply only at some particular concentration. It seems advantageous to make comparisons over a concentration range, and so to choose the range that the simpler mathematical relationships will hold. For this purpose Freundlich's adsorption isotherm and the equation of Langmuir for simple adsorption have been employed.

The Freundlich equation

The empirical equation proposed by Freundlich for the adsorption isotherm has been commonly used. Though it is undoubtedly only approximately correct, it fits much of the published data fairly well. Freundlich (5) himself has pointed out that for solutions the equation is not a complete formula covering all concentrations, for it is based on the apparent adsorption of the solute molecule, and adsorption of the solvent is not taken into consideration. Fodor and Schönfeld (4) and Pavlov (31) find that n varies with dilution and amount of carbon used. Garner (10) likewise demonstrated the limited range of application of the isotherm. In some preliminary experiments we tested adsorption from fairly dilute solutions. Over the range from 0.001 to 0.01 molar equilibrium concentrations, the values for the amount adsorbed were low as compared with equilibrium concentrations above 0.01 molar. For this reason initial concentrations were so chosen that the concentration at equilibrium would generally be between 0.01 and 0.25 molar. The logarithmic values for C and the corresponding values of a between these limits approximate a straight line.

Values for $1/n$ and α of the equations were calculated by the method of least squares applied to the logarithmic equation. Table 1 lists these constants, the number of points considered, and the average error between observed values and those calculated from the equation. The "average error" is the percentage difference between the various observed values and the values at comparable concentrations as given by the fitted equation. The agreement between the observed values of the adsorbed and the calculated is excellent, as evidenced by the average per cent error. The logarithmic curves in the graphs also show how nearly the values fall on the calculated straight lines.

The constants $1/n$ and α have no simple physical meaning. The equation, at best, can serve only to calculate the millimoles adsorbed for any equilibrium concentration within the range over which the relationship holds. Only the fatty acids display any regularities. From formic

TABLE 1

Showing values of "$1/n$" and "α" of the Freundlich equation, $a = \alpha C^{1/n}$ for the various systems of Norite and organic acid at equilibrium, as well as the average per cent error and the number of points used for the calculations

ACID	α	$1/n$	AVERAGE PER CENT ERROR BETWEEN OBSD. AND CALCD. a	NUMBER OF POINTS
Formic	2.47	0.435	2.6	15
Acetic	2.46	0.351	2.6	18
Propionic	2.46	0.236	1.8	15
n-Butyric	2.46	0.177	2.3	15
n-Valeric	2.84	0.182	2.8	12
Caproic	3.03	0.175	1.8	11
Isobutyric	2.36	0.273	12.3	10
Isovaleric	2.51	0.227	2.6	9
Glycolic	1.54	0.390	4.1	13
Lactic	1.66	0.335	3.6	18
Glyceric	1.29	0.267	6.7	13
Glyoxylic	3.89	0.455	2.3	12
Pyruvic	2.44	0.273	3.5	15
Levulinic	1.83	0.183	2.9	8
Oxalic	3.62	0.551	4.9	29
Malonic	3.88	0.410	3.3	11
Succinic	2.83	0.303	4.3	16
Glutaric	1.96	0.201	5.1	13
Adipic	1.79	0.163	4.5	22
Malic	1.28	0.252	2.2	15
Tartaric	0.94	0.275	3.3	15
Maleic	1.90	0.203	2.9	14
Fumaric	2.81	0.248	4.6	9
Mesaconic	1.80	0.133	2.4	14
Citraconic	1.69	0.167	1.8	15
Itaconic	1.54	0.148	1.9	15
Methylsuccinic	1.30	0.172	1.6	14
Citric	0.73	0.203	3.3	8
Monobromosuccinic	1.82	0.195	2.0	9
Dibromosuccinic	2.58	0.320	2.2	8

through butyric acids the value of α is constant and from butyric through caproic acids the slope of the logarithmic curves is also constant (see figure 1). Any other attempt to interpret the α and $1/n$ of table 1 in terms of structural relationships is unfruitful.

The Langmuir equation (22)

By the usual rearrangement of this equation

$$\frac{C}{a} = \frac{1}{\alpha\beta} + \frac{C}{\beta} \qquad (1)$$

the values of the constants α and β are determinable by plotting C/a against C. These constants were calculated from our data by the method

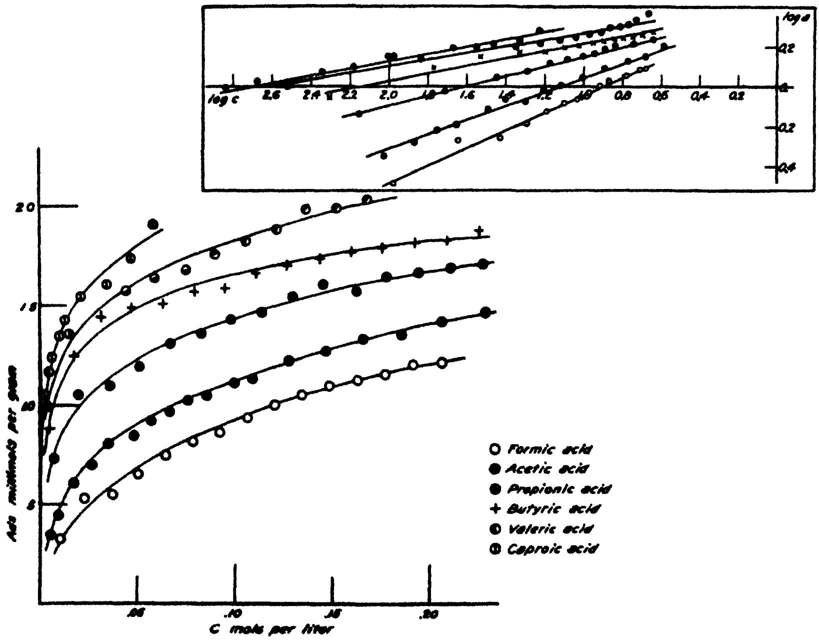

FIG. 1. ADSORPTION ISOTHERMALS FOR THE HOMOLOGOUS SERIES OF THE FATTY ACIDS

In the graph on the lower left the values are plotted arithmetically; in the one on the upper right, logarithmically.

of least squares. When plotted straight lines resulted in all cases. As with the Freundlich equation, the Langmuir relationship was not found to hold in very low concentrations; in fact the range over which the equation was applicable was slightly narrower than for the Freundlich equation. The Langmuir equation is applicable over the range corresponding to equilibrium concentrations of 0.02 to 0.22 molar. The average per cent error (table 2) is the error within this range.

TABLE 2

Showing values of α *and* β *of the Langmuir equation,* $a = \frac{\alpha\beta C}{1 + \alpha C}$ *for various systems of Norite and organic acid at equilibrium*

Columns 5 and 6 give the average per cent error over the range for which the Langmuir equation holds, together with the number of points considered

ACID	$\alpha\beta$	α	β	AVERAGE PER CENT ERROR BETWEEN OBSD. AND CALCD. a	NUMBER OF POINTS
Formic	0.273	0.159	1.710	1.0	13
Acetic	0.462	0.266	1.736	7.0	16
Propionic	0 925	0.491	1.885	2.0	13
Butyric	1 689	0 863	1.957	2.0	13
Valeric	1.878	0 872	2.154	5 8	11
Caproic	8 772	4.636	1.892	5.4	7
Isobutyric	0 883	0.497	1.776	5.5	7
Isovaleric	1.630	0 902	1 807	5.1	7
Glycolic	0.239	0 249	0 958	5.1	12
Lactic	0.437	0 415	1.054	4.0	18
Glyceric	0 668	0.812	0.823	8.5	13
Glyoxylic	0.508	0 223	2 275	3.0	11
Pyruvic	0 979	0.585	1 674	2 8	14
Levulinic	2 990	2 289	1.307	3.4	6
Oxalic	0 440	0.332	1 325	3 7	29
Malonic	1 897	1 540	1.232	5 6	11
Succinic	0 865	0 467	1 854	6 0	16
Glutaric	3 697	3 104	1 192	4 8	13
Adipic	2 347	1 886	1 245	4 5	19
Malic	0.531	0.574	0 927	2 3	14
Tartaric	0 322	0 468	0.687	2.5	14
Fumaric	7.097	5 798	1.224	4.1	9
Maleic	1 233	0 884	1 395	3.6	14
Mesaconic	2 706	1 886	1.435	2.9	14
Citraconic	1 356	1.014	1 337	4 7	14
Itaconic	1.167	0.904	1.291	4 0	14
Methylsuccinic	0 664	0 608	1.092	4.2	14
Citric	1.444	2 757	0.524	11 7	8
Monobromosuccinic	0 934	0.643	1.451	3.0	8
Dibromosuccinic	1.397	1.119	1.248	3.6	8

Langmuir's equation is more useful than the Freundlich adsorption isothermal for the latter is the analytical expression for the general parabola, while the former is that of a rectangular hyperbola passing through the origin. Hence, Langmuir's equation tends to a definite limit for the adsorption of the solute on the surface, while with Freundlich's equation the adsorption theoretically increases indefinitely with increasing concentration. It should accordingly be possible to use either the constants α or β of the Langmuir equation for comparison of the acids, especially since these constants have some physical significance. For comparisons of structural relationships we have used the constant β, which is equal to a (the amount adsorbed) when C (equilibrium concentration) is a maximum.

Interpretation of Traube's rule

Freundlich (reference 6, pp. 195–6) stated Traube's rule as applied to adsorption in the following manner: "The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series." He applied this rule to the first four members of the fatty acid series, calculating the ratio $\frac{a_{n+1}}{a_n}$ at a given C (0.1 mole per liter). The value of the ratio was found to be approximately 1.5. For the ratio $\frac{C_n}{C_{n+1}}$, where $a = 1.26$ millimoles per gram of charcoal an approximate constancy of 2 to 3 was obtained. Many workers have since confirmed Freundlich's generalities. However, the comparison of ratios at any one concentration or any one value for the amount adsorbed should not of necessity give a constant value. It has already been pointed out that logarithmic isotherms (cf. figure 1) for formic, acetic, propionic, and butyric acids tend to meet at a common point, and that those for butyric, valeric, and caproic acids have a constant slope and are, therefore, parallel over the range studied. Further, it is evident from a study of the β of the Langmuir relationship that this homologous series of organic acids tends to approach a constant value of about 1.9 millimoles per gram of adsorbent. Calculations were made for the value of C at various concentrations by means of the Freundlich adsorption isothermal. The ratios $\frac{C_n}{C_{n+1}}$ were then calculated. They are shown in table 3. The values here fluctuate as one might expect from a knowledge of the constants. It is clear, too, that at higher values of a the ratio tends to become more nearly constant, and that the constant is somewhat lower than the ratio obtained by Freundlich. He reports an approximate constancy of about 2 to 3 at a single value of a of 1.26 millimoles per gram. In a similar manner values of C were chosen, and ratios between the corresponding values of a

were calculated for the Freundlich adsorption isotherm. The calculations are shown in table 4. The agreement is better for such a ratio than it is in the case of the $\frac{C_n}{C_{n+1}}$ ratio. The value of q tends to be more nearly constant as the equilibrium concentration approaches 0.25 molar.

TABLE 3

Showing the ratios of $\frac{C_n}{C_{n+1}}$ *for various fatty acids at various values of a on the ordinate of their respective Freundlich adsorption isotherms*

ADSORBED SUBSTANCE	C IN MOLES PER LITER WHEN							
	$a = 1.00$	q*	$a = 1.179$	q*	$a = 1.500$	q*	$a = 1.978$	q*
Formic	0.125		0.182		0.317			
Acetic	0.077	1.63	0.122	1.49	0.243	1.31		
Propionic	0.022	3.48	0.044	2.78	0.123	1.98	0.398	
Butyric	0.006	3.58	0.015	2.85	0.061	2.02	0.297	1.34
Valeric	0.004	1.88	0.008	1.93	0.030	2.01	0.126	2.35
Caproic	0.002	1.84	0.005	1.77	0.018	1.67	0.088	1.43

* $q = \frac{C_n}{C_{n+1}}$.

TABLE 4

Showing the ratios of $\frac{a_{n+1}}{a_n}$ *for various fatty acids at various values of C (the equilibrium concentration) on the abscissa of their respective Freundlich adsorption isotherms*

ADSORBED SUBSTANCE	a IN MILLIMOLES PER GRAM WHEN									
	$C = 0.01$	q*	$C = 0.025$	q*	$C = 0.088$	q*	$C = 0.10$	q*	$C = 0.25$	q*
Formic	0.33		0.50		0.86		0.91		1.35	
Acetic	0.49	1.47	0.68	1.36	1.05	1.22	1.09	1.21	1.52	1.12
Propionic	0.83	1.70	1.03	1.53	1.39	1.32	1.43	1.31	1.77	1.17
Butyric	1.09	1.31	1.28	1.24	1.60	1.15	1.64	1.15	1.92	1.09
Valeric	1.23	1.12	1.44	1.13	1.82	1.14	1.87	1.12	2.20	1.14
Caproic	1.35	1.10	1.59	1.10	1.98	1.09				

* $q = \frac{a_{n+1}}{a_n}$.

Relationships over a range of concentration should be more significant than at isolated concentrations. Such relationships may be secured by using the areas under the curves, i.e., for $\frac{C_n}{C_{n+1}}$ we have $\frac{\text{Area } (C)_{n+1}}{\text{Area } (C)_n}$ for the curves a plotted against C; for $\frac{a_{n+1}}{a_n}$ we have $\frac{\text{Area (a)}_n}{\text{Area (a)}_{n+1}}$ for the curves C plotted against a. The relationships

$$\text{Area } (C) = \int_a^b \alpha C^{1/n}\, dC \tag{2}$$

and

$$\text{Area } (a) = \int_a^b (a/\alpha)^n\, da \tag{3}$$

were used. Employing equation 2 between the limits 0.01 and 0.06 (approximate solubility limit of caproic acid) and between 0.01 and 0.25, the values in table 5 and table 6 were obtained.

TABLE 5

The values for Area $(C) = \int_{0.01}^{0.06} \alpha C^{1/n} dC$ *for adsorption isotherms of the various fatty acids*

SUBSTANCE ADSORBED	AREA (C)	RATIO: $\frac{\text{AREA } (C)_{n+1}}{\text{AREA } (C)_n}$
Formic	0 0281	
Acetic	0 0371	1 32
Propionic	0 0549	1 48
Butyric	0 0671	1 22
Valeric	0 0760	1 13
Caproic	0 0831	1 09
Average		1 25

These calculations show more definite constancy. The constant is approximately 1.2 and as an average ratio is lower than Freundlich's value of 2 to 3.

Using equation 3 between the limits 1.06 and 1.9, we obtain the data shown in table 7. Except for the first ratio these average values are approximately constant and equal approximately 1.8, which is in general agreement with Freundlich's value for a single point of 1.5.

The constants of Langmuir's equation

In a discussion of the liquid-gas interface Freundlich (reference 7, pp. 76–9) combines the Szyszkowski equation and the Gibbs equation and shows that

$$a = \frac{b\sigma}{RT} \frac{C}{C + k} \tag{4}$$

where a = amount adsorbed, σ = the surface tension of the solvent, C = equilibrium concentration, and b and k are constants. Now Langmuir's equation may be written

$$a = \frac{\beta C}{1/\alpha + C} \tag{5}$$

TABLE 6

The value of Area $(C) = \int_{0.01}^{0.25} aC^{1/n}dC$ *for adsorption isotherms of various fatty acids excluding caproic acid*

SUBSTANCE ADSORBED	AREA (C)	RATIO: $\frac{\text{AREA } (C)_{n+1}}{\text{AREA } (C)_n}$
Formic	0.233	
Acetic	0.276	1.19
Propionic	0.352	1.28
Butyric	0.400	1.13
Valeric	0.456	1.14
Average		1.19

TABLE 7

The value Area $(a) = \int_{1.06}^{1.90} \left(\frac{a}{\alpha}\right)^n da$ *for adsorption isotherms of various fatty acids*

ADSORBED SUBSTANCE	AREA (a)	RATIO: $\frac{\text{AREA } (a)_n}{\text{AREA } (a)_{n+1}}$
Formic	0.269	
Acetic	0.211	1.28
Propionic	0.116	1.82
Butyric	0.065	1.79
Valeric	0.032	2.05
Caproic	0.019	1.63

Hence, it is apparent that

$$\beta = \frac{b\sigma}{RT} \tag{6}$$

and

$$\frac{1}{\alpha} = k \tag{7}$$

But $k = \frac{1}{q}$ where q is the capillarity. Therefore we see that $\alpha = q$ (the capillarity). The dimensions of the constant β are of interest. σ is defined as force $\left(\frac{M}{T^2}\right)$, RT has the dimensions of energy $\left(\frac{ML}{T^2} \times L\right)$, and b can be proved to be a pure number. Therefore,

$$\beta = \frac{1}{L^2} \tag{8}$$

Accordingly β has the dimensions of the reciprocal of surface. It follows from the development above, that β will serve as a more logical basis for comparisons to be made than will α.

TABLE 8

Showing agreement between the experimentally determined values of β and the calculated values of a (at maximum adsorption) when C_e (equilibrium concentration) is that of a saturated solution

ACID	C_e IN MILLIMOLES PER 75 CC	β	a (MAXIMUM) IN MILLIMOLES PER GRAM	PER CENT ERROR
Valeric	27 19	2 154	2 068	4.1
Caproic	6 60	1 892	1 862	1.6
Isobutyric	170 33	1 776	1 755	1.2
Isovaleric	31 13	1 807	1 745	3 5
Oxalic	97 92	1 325	1 286	3 2
Malonic	542.18	1 231	1 232	−0 1
Succinic	52 22	1.854	1 781	4.0
Glutaric	391 87	1 192	1 191	0.1
Adipic	8 11	1 245	1 169	6 0
Tartaric	696 23	0 687	0 685	0 7
Fumaric	4 52	1.224	1 179	3.7
Maleic	509.33	1.395	1.392	0.2
Mesaconic	20 55	1.435	1.399	2.5
Itaconic	53 11	1 291	1.265	2 0

Determination of values for maximum adsorption and the corresponding equilibrium concentration

If the a of Langmuir's equation is differentiated with respect to C, it becomes obvious that a will equal β when $\frac{da}{dC}$ equals zero, and this will be true when the slope of the isotherm approximates 0°. However, the determination of C for maximum a presents difficulties. From a purely theoretical standpoint it would seem that a should approach a maximum when C equals the concentration of a saturated solution of the acid. Such concentrations were substituted in our calculated Langmuir equations and were compared with β for the corresponding acid. Taking only compounds which have a limited solubility the values shown in table 8 were secured. This table shows remarkable agreement between the determined and calculated values, indicating that the theory discussed above has a sound basis.

Another possible method of demonstrating the validity of the assumption of maximum adsorption when the equilibrium concentration is that of a saturated solution, is by a graphical device adapted from theoretical considerations of Polanyi and Goldman (34). In dealing with adsorption of vapors Polanyi and Goldman calculated "affinities" from the general relationship

$$A_x = RT \ln \frac{P_s}{P_x} \tag{9}$$

where P_s is vapor pressure of the pure substance at the temperature T, P_x is the equilibrium pressure obtained in adsorption studies. They plotted the values of A_x for a given P_x against the values for adsorption obtained at this equilibrium pressure. Curves were obtained which were all similar in character and were displaced slightly by changes in temperature. In a later paper Polanyi and Heyne (35) considered isothermals for "substances in solution." Here the affinity is represented by

$$A_x = RT \ln \frac{C_s}{C_x} \tag{10}$$

where C_s is the solution saturation value for the compound and C_x is any other lower concentration. When Polanyi and Heyne calculated A_x from equilibrium concentrations and plotted the resulting values against the a in millimoles per gram corresponding to that C, the same types of curves were obtained in the case of solutions as in the case of vapors. It is obvious from equation 10 that when $C_s = C_x$, $A_x = 0$. Hence, by extrapolation of the curves (see figures 2, 3, 4, 5, 6), one obtains values for a when A_x is zero. This should represent the "saturation value." It should be said at this point that Polanyi obtained similar curves regardless of the solvent used and that in all cases the substances to which he applied his treatment had a limited solubility. Increased temperature displaced the curves slightly in the direction of higher A_x.

In the present study affinities were calculated in calories for all acids used excluding only those which are infinitely soluble (miscible in all proportions). In the case of *n*-valeric, caproic, isovaleric, succinic, adipic, fumaric, mesaconic, and itaconic acids when the values were plotted and the curves extrapolated, values for a when $A_x = 0$ were within good agreement with β. Curves of all other acids for the most part tended to become practically asymptotic to the a-axis and no extrapolation was possible. In some cases (oxalic acid, figure 2) *straight lines* were obtained which could be extrapolated, but the values for the amount adsorbed were some 25

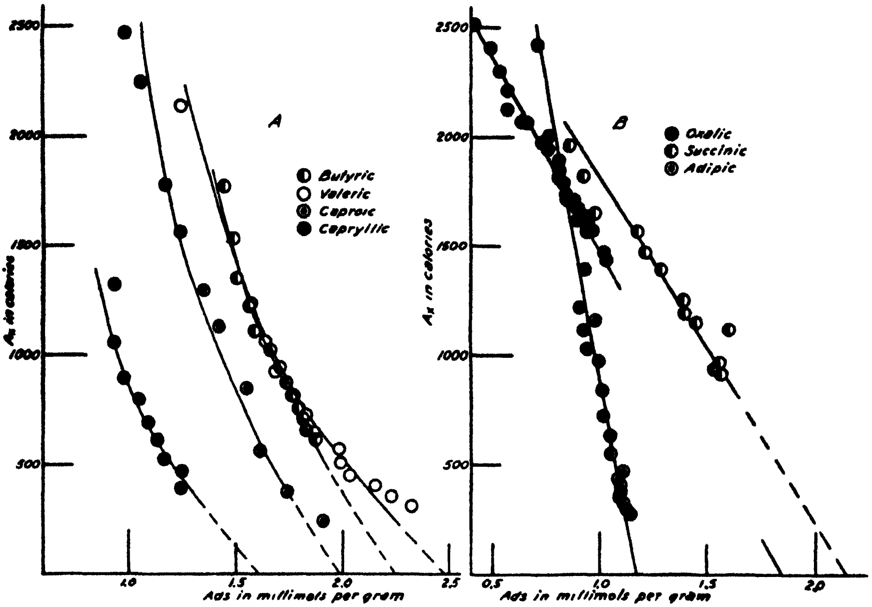

FIG. 2. THE AFFINITY CURVES OF THE MONO- AND DI-CARBOXYLIC ACIDS

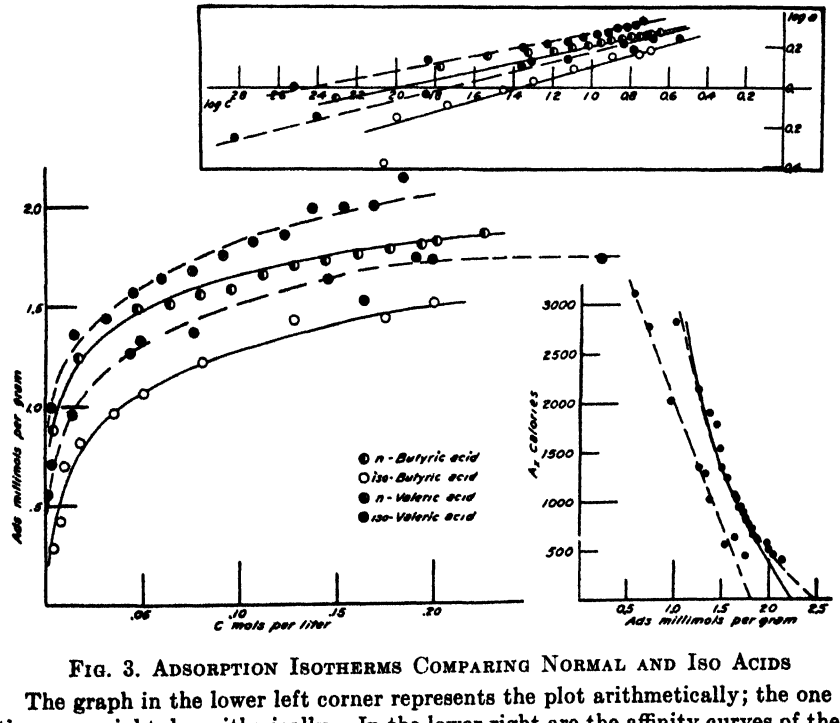

FIG. 3. ADSORPTION ISOTHERMS COMPARING NORMAL AND ISO ACIDS

The graph in the lower left corner represents the plot arithmetically; the one in the upper right, logarithmically. In the lower right are the affinity curves of these acids.

to 30 per cent higher than the experimentally determined values. In the case of butyric acid, however, activity coefficients (Parks and Huffman (30) were applied so that equation 10 becomes

$$A_x = RT \ln \frac{C_s\gamma_s}{C_x\gamma_x} \tag{11}$$

On plotting the values for butyric acid obtained through equation 11 extrapolation was possible and a value in approximate agreement with β

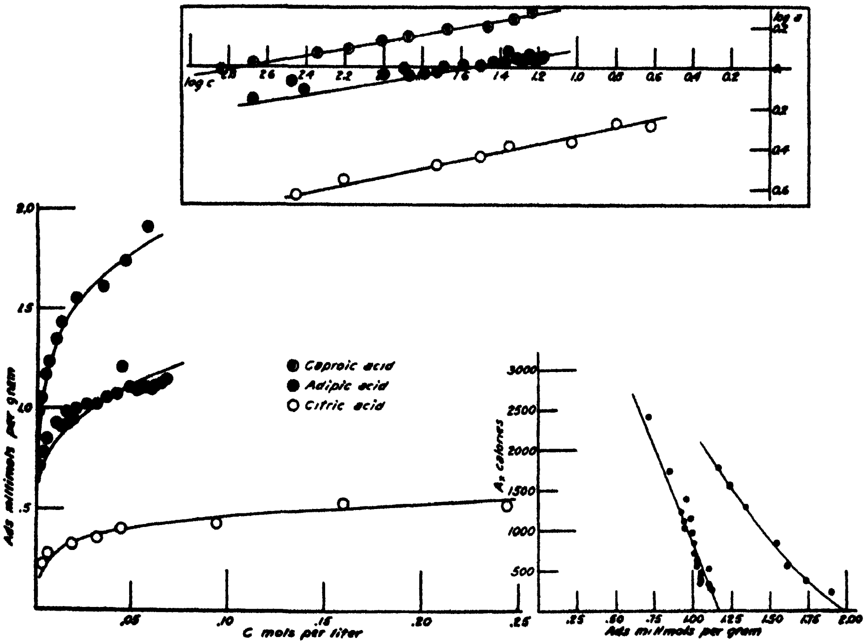

FIG. 4. ADSORPTION ISOTHERMALS FOR THE ACIDS HAVING THE SAME NUMBER OF CARBON ATOMS BUT DIFFERING IN THE NUMBER OF CARBOXYL GROUPS

In the graph in the lower left of the figure values are plotted arithmetically; in the upper right, logarithmically. The graph in the lower right represents the affinity curves for caproic and adipic acids.

and a maximum was obtained. The extrapolated values from the curves are listed in table 9 together with β and a maximum as calculated when the equilibrium concentration is that of a saturated solution (cf. table 8).

Calculation of cross-sectional areas of adsorbed molecules

The data in table 2 show that the values of the β of the Langmuir equation follow, relatively, the same general trends when comparisons are made between structurally related homologous series. It has already been shown that β has the dimensions of surface. The value represents the maximum adsorption. If one makes certain assumptions it should be possible to calculate the approximate area possessed by 1 g. of Norite and from this area, in turn, to approximate the area occupied by the molecules of the various acids when adsorbed on the Norite. Ockrent (27, 28), following a slightly different method, has utilized Langmuir's equation for determining areas of molecules adsorbed on carbon.

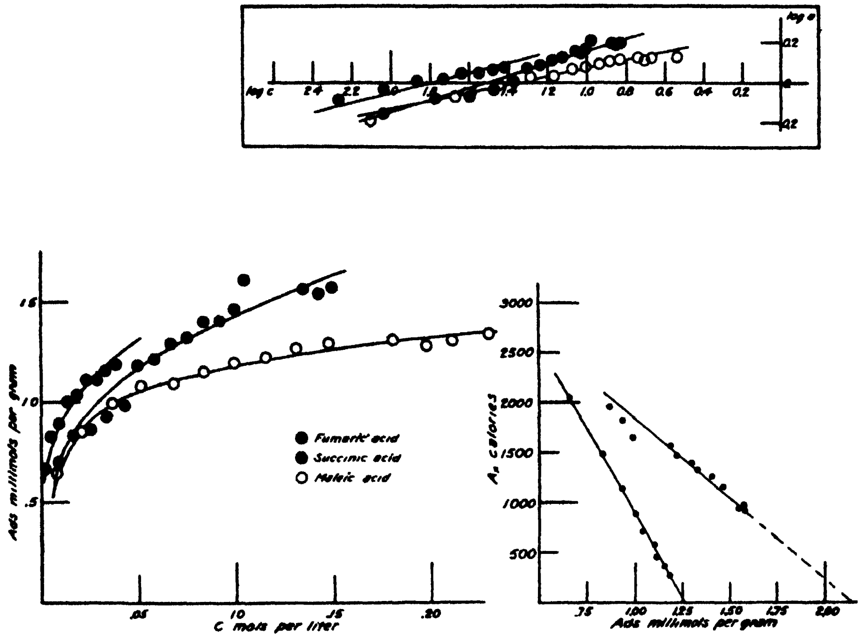

FIG. 5. ADSORPTION ISOTHERMALS SHOWING THE EFFECT OF THE DOUBLE BOND AND OF *cis* AND *trans* ISOMERISM ON ADSORPTION

The graph in the lower left of the figure represents the curves for values plotted arithmetically; in the upper right, logarithmically. Affinity curves for fumaric and succinic acids are given in the lower right of the figure.

The method employed in the present study was to make use of the experimentally determined β, the maximum adsorption values for each acid under our experimental conditions. Accordingly the areas calculated apply with certainty only to this study and may not represent the absolute areas. It is believed, however, that they are valid for comparison *inter se*. The assumptions upon which the calculations were based are: (1) At maximum adsorption a monomolecular layer is formed. (2) The fatty acids have approximately the same adsorption maximum. (3) The average β (1.889) of these acids represents the millimoles adsorbed per gram of adsorbent in the monomolecular film. (4) The molecules of the various sulted from studies on a single and comparable substrate. Subject to the assumptions made, it is seen from table 10 that the affinities of the molecules for water and the orientation of the molecules at the liquid-carbon interface is altered by the introduction of specific polar groups, so that the areas occupied in the interface by the molecules of the structurally different organic acids are varied, whereas structurally similar organic acids tend to approximate similar areas.

The ratios in table 11 are interpreted as representing the relative areas taken up at the interface by the different solute molecules. There is relatively little variation between the areas calculated for the iso acid as compared with that assumed for the normal acid. The dicarboxylic acids occupy approximately 1.5 times the area of the monocarboxylic acids, with the notable exception of succinic. This latter compound is apparently oriented at saturation in a fashion similar to the monocarboxylic acids, since the area per molecule (21.4 sq. A.U.) differs inappreciably from the average of the latter. The effect of the first hydroxyl group added to the straight chain of the fatty acids and succinic acid increases the area by twice the original value. As is to be expected, the effect of the second hydroxyl is greater than that of the first, and is approximately 2.5 times that of the straight hydrocarbon chain. The introduction of a double bond has lessened the adsorption (increased the polarity), as anticipated, as is shown by a comparison of succinic, fumaric and maleic acids.

TABLE 11

Summary of approximation in table 10

ADSORBATE	MEAN VALUE	PER CENT ERROR BETWEEN MEAN AND	
		Low value	High value
Fatty acids	21*		
Iso acids	22	0.9	0.9
Dicarboxylic acids†	32	2.1	4.1
Monohydroxy acids	41	8.3	4.4
Dihydroxy acids	53	9.1	8.9
Geometric isomers (unsaturated)	30	5.5	7.7

* Assumed value.

† Succinic excepted.

The ratios are as follows:

(1) Normal fatty acids: iso acids = 1:1.
(2) Normal fatty acids: dicarboxylic acids = 1:1.5.
(3) Acid: monohydroxy acid: dihydroxy acid = 1:2:2.5.

Comparison of the β of the Langmuir equation of the mono- and di-carboxylic acids with their melting points

An examination of the values of β of the dicarboxylic acids (table 2) reveals an alternation in values between successive members of homologous series. This is also true, as has long been known, of both the solubilities and melting points of the members of these series. When the values of β (table 2) are plotted against the number of carbon atoms in their corresponding acids and the points representing the "odd" and "even" acids are connected it will be observed that the curves so produced (figure 7) are very similar to those obtained either from melting point or solubility data. The

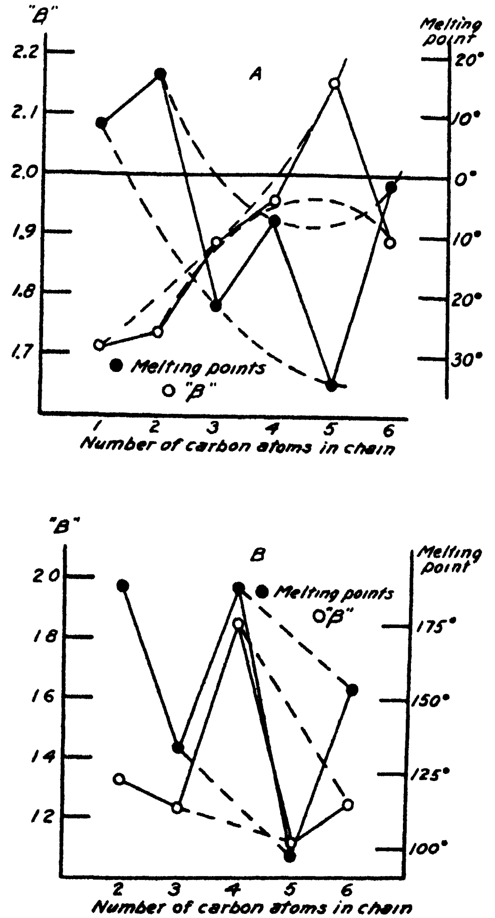

FIG. 7. SHOWING THE ALTERNATIONS IN THE VALUES OF β (LANGMUIR'S EQUATION) AND THOSE OF THE MELTING POINTS FOR HOMOLOGOUS SERIES OF THE MONO- AND DI-CARBOXYLIC ACIDS

A, the monobasic fatty acids; B, the dibasic acids results in themselves perhaps are not particularly striking, but when comparison is made with curves drawn from similar data of the homologous series of the fatty acids it becomes apparent that there is some significant relationship between the melting points and β. Figure 7A shows these relationships. In the case of the fatty acids the plot of β against the number of odd carbon atoms (1, 3, 5) produces a line which is similar in general trend, although opposite in direction to the line produced by plotting the 1, 3, 5 carbon atoms against the melting points of the compounds. The same is true for the lines plotted for carbons 2, 4, 6 against β and carbons 2, 4, 6 against melting points. These observations likewise hold for the dicarboxylic acids (figure 7B).

The *alternation in melting points* is characteristic of the *solid state* of both the mono- and di-carboxylic acids. In the case of the higher fatty acids Garner and Randall (8) and Garner and Ryder (9) have shown that between odd and even acids alternation is more characteristic of the crystalline state than of the liquid state. They have shown such alternation in specific heat and molecular volume. Jensen and Gortner (18) report an odd-even carbon atom effect for the electrokinetic potential of homologous series of the lower members of the normal fatty acids, and their esters at an organic liquid-Al_2O_3 interface. Müller and Shearer (26) have suggested on the basis of x-ray studies that the molecules in the crystal are arranged end to end in opposite directions. Garner and Randall (8) carry this suggestion further and speculate as to possible arrangements similar in character to orientation. In respect to the nature of thin films of higher fatty acids at an interface Rideal (37) says: "The behavior of the higher fatty acids in thin films may well be compared with that of smectic or string-like anisotropic crystalline liquids: these liquids consist of molecules of a chain type and exhibit the property of orientation." The present study adds confirmation to the view that not only do the higher fatty acids in thin films possess this "crystalline" structure, but that the lower members of the series, too, as thin films adsorbed on a solid interface, are held there in "crystalline" form, and probably in the form of a *solid*, close-packed oriented layer of molecules. It is interesting to note that the "liquid" fatty acids, as well as the "liquid" esters studied by Jensen and Gortner (18), when adsorbed at an interface are apparently in the *solid state*.

IV. DISCUSSION

Difficulties attending attempts at comparison from too limited data

Earlier in this paper attention has been called to the fact that results obtained by making comparisons at only one equilibrium concentration do not necessarily represent values which would be obtained over a range of concentrations and that they may be valid only at the point chosen.

For example Shilov and Nekrassov (41) have published data on the per cent adsorption of an homologous series of the fatty acids and the dibasic acids. The fatty acids were studied at an initial concentration of $M/100$, the dibasic acids at a concentration of $M/200$. Their data are shown in table 12 where their values for per cent adsorbed and the difference between successive members of the homologous series are recorded.

TABLE 12

Values from data of Shilov and Nekrassov (41) for the "per cent adsorbed" and the differences between successive members of an homologous series*

($C_1 = M/100$)	FATTY ACIDS	
	A*	($A_{n+1} - A_n$)
Formic	13.3	
Acetic	16.0	2.7
Propionic	22.3	6.3
Butyric	25.5	13.2
Valeric	51.3	15.8
Caproic	67.1	15.8
Caprylic	78.4	11.3

* "Per cent adsorbed" $= A = \frac{C_1 - C_2}{C_1} \times 100$ where C_1 = initial concentration and C_2 = equilibrium concentration.

TABLE 13

Values for "per cent adsorbed" obtained from calculations comparable to those of Shilov and Nekrassov (recorded in table 12) for acetic and propionic acids, utilizing data of this study

C_1	A		$A_{n+1} - A_n$
	Acetic acid	Propionic acid	
0.02	2.65	4.04	1.39
0.04	1.86	2.54	0.68
0.06	1.46	1.92	0.46
0.08	1.24	1.59	0.35
0.10	1.08	1.37	0.29
0.15	0.83	1.03	0.20
0.20	0.68	0.83	0.17
0.25	0.57	0.69	0.08

Table 13 shows comparable calculations made from our data on acetic and propionic acids. It will be observed that, whereas Shilov and Nekrassov found a value of 16 per cent adsorption for acetic acid and 22.3 per cent for propionic acid with a difference of 6.3 per cent, the more extensive series of data taken over a range of concentration yield values for acetic acid varying from 2.7 to 0.6 per cent and for propionic acid from 4.0 to 0.7 per cent with differences of 1.4 to 0.08 per cent. Obviously single point observations may lead to erroneous conclusions.

Furthermore, in figure 8, acetic and glyoxylic acids present an interesting example. If comparison is made at from 0.01 to 0.03 molar equilibrium concentration, one would say that the two were adsorbed to about the same extent within experimental error. Above these values the two curves sharply diverge from each other. Again, if one applied a basis for comparison on the per cent adsorbed, it is evident that the values would be widely divergent at 0.03 and 0.25 molar concentration. The curves for the dicarboxylic acids (figure 9) present the same general difficulties. Below 0.025 molar equilibrium concentration, the adsorption of the members of the series increased definitely with increasing number of carbon atoms. It is plainly evident from figure 9 that above this concentration this is no longer true, and that with the exception of oxalic acid points may be chosen by means of which no essential change in adsorption between one member and the next higher member can be demonstrated. The last

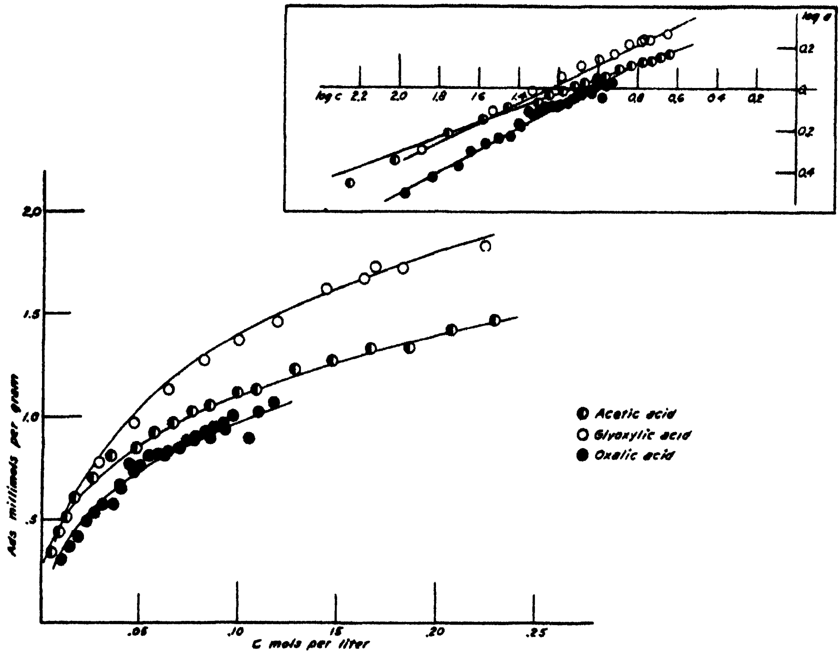

FIG. 8. ADSORPTION ISOTHERMALS FOR ACETIC, GLYOXYLIC, AND OXALIC ACIDS, SHOWING THE EFFECT OVER A DEFINITE CONCENTRATION RANGE OF SUBSTITUTING THE ALDEHYDE AND CARBOXYL GROUPS FOR THE METHYL GROUP

In the graph in the lower left of the figure the values are plotted arithmetically; in the upper right, logarithmically.

case which will be cited refers to figure 5 in which isotherms for succinic, maleic, and fumaric acids are given. Langmuir (21) and Harkins (14, 15) have pointed out that the double bond increases the polarity of the compound. This should mean decreased adsorption of maleic acid and its *trans*-isomer, fumaric acid, when these are compared with succinic acid. Our data show that over the range studied maleic acid is less adsorbed than is succinic, but that fumaric acid is more greatly adsorbed up to the limits of its solubility. Furthermore, Alekseevskii (1) from a few series of point studies came to the conclusion that fumaric acid is always more greatly adsorbed than is maleic. In general, our data substantiate this, yet one cannot but feel that such comparisons, although they may possess validity, are not so desirable as those made when the surface is saturated, i.e., when the equilibrium concentration is that of a saturated solution. Comparisons of β which give the maximum amount adsorbed show that a smaller number of millimoles of the acids, fumaric and maleic, is adsorbed per gram of adsorbent when the surface is "full" than is the case with succinic acid. This is in accord with the ideas of Langmuir and Harkins. Further, we find on the basis of our assumptions that fumaric and maleic acids

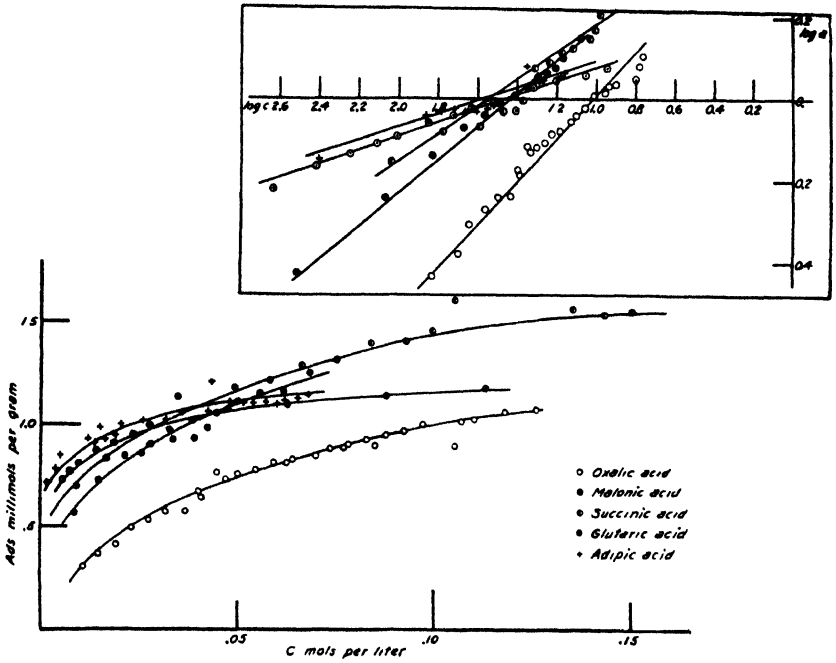

FIG. 9. ADSORPTION ISOTHERMALS FOR THE DICARBOXYLIC ACIDS

In the graph on the lower left the values are plotted arithmetically; in the one on the upper right, logarithmically.

are about equally adsorbed at saturation, since they vary only some 0.17 millimole per gram of adsorbent. It seems more logical, therefore, to attempt to make comparisons when adsorption is at a maximum as we have already done, for while one must grant the accuracy of "single point" studies it must be admitted that they can hardly lend themselves to a general study of structural comparisons.

The arrangement of molecules in the interface

The assumptions on which the calculations of the cross-sectional areas are based have been stated. It was our intention to point out by a statement of these assumptions that values obtained are purely *relative* among themselves and may not represent absolute areas. We have pointed out, however, that the surface area of the adsorbent obtained by calculation is within the range of other experimental values. Paneth and Radu (29) report values for various carbons varying from 46.2 to 268.0 square meters. The value obtained in these experiments for Norite is 240 square meters.

Bearing in mind the relative character of the values reported in table 9, we can only theorize as to the nature of the arrangement of molecules on the surface. The assumption has been made that the cross-sectional area possessed by the fatty acids is 21 sq. A.U. Such an area may be predicted by the head group when the adsorbent surface is filled. It seems likely on comparing the relative areas of isobutyric and isovaleric acids with butyric and valeric acids, respectively, that only one $—CH_3$ is held at the solid interface and that the —COOH group in the water determines the area. The ratio between the cross-sectional areas of the normal and iso acids is approximately 1:1. Alekseevskii (1) has pointed out that the normal acids are of such a structure that the —COOH or $—CH_3$ may be at the surface, so that at complete filling there will be a larger adsorption of the normal than of the iso acid. He concludes this from a study of two series made from initial concentrations of 0.28 and 0.43 molar solutions. Shilov and Nekrassov (41) by a similar type of experimentation have shown iso acids to be less adsorbed than normal acids. We believe, however, that our data more nearly show what condition is approximately approached at complete filling.

With the exception of succinic acid the dicarboxylic acids have an average covering of the surface of the adsorbent of about 30 sq. A.U. This value is about 1.5 times that of the monocarboxylic acids. At saturation, then, could one not consider that two carbon atoms are in the surface of the adsorbent with the —COOH groups out into the aqueous phase? There are two possible explanations, which are perhaps interdependent, for the fact that in such an arrangement the area is not twice that of a monocarboxylic acid. The forces holding the two carbon atoms together are primary valence forces, and because of them the two carbons in the molecule are in much closer proximity than are adjacent carbon atoms of two molecules of the monocarboxylic acids. Then again, it may be that the alignment of surface forces is such that only a portion of them can be effective in the case of the dicarboxylic acids. The latter reasoning is weak, perhaps, because there is apparent regularity between the differences the values demonstrate. Why succinic acid is oriented apparently in the same fashion as the monocarboxylic acids is unanswerable in view of the above. Another indication of orientation of such a type as discussed with

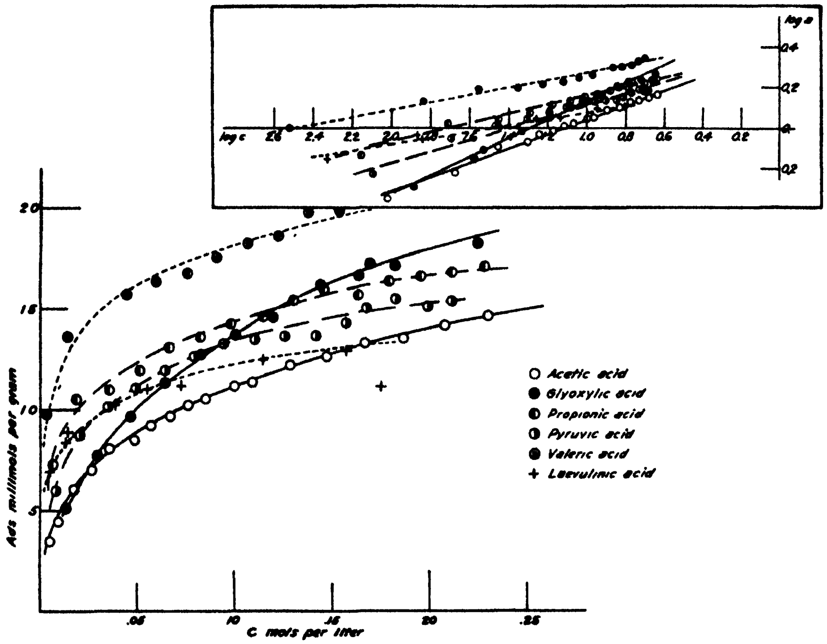

FIG. 10. ADSORPTION ISOTHERMALS COMPARING ACETIC, PROPIONIC, AND VALERIC ACIDS WITH THEIR RESPECTIVE ALDEHYDE OR KETO DERIVATIVES

The graph in the lower left of the figure represents the values plotted arithmetically; in the upper right, logarithmically.

the dicarboxylic acids is the behavior of citric acid. This acid is adsorbed to a much lesser extent than is adipic acid, which contains the same number of carbon atoms. The ratio between caproic, adipic, and citric acids all containing the same number of carbon atoms is approximately 2:3:7.5. It appears probable that the molecule of citric acid is held to a greater degree along its length with the polar groups oriented out into the aqueous phase.

We find that glyoxylic acid at saturation takes up a smaller relative area than does acetic acid, from which it is derived. Surely one should assume that the substitution of the aldehyde group for the methyl group of acetic acid will increase the polar character of the molecule and that, therefore, a smaller quantity should be adsorbed. The maximum adsorbed quantity for acetic acid is 1.74 millimoles per gram of adsorbent, while that for glyoxylic is 2.28. The only accounting for such a difference must be on the basis of closer packing of the glyoxylic molecules in the interface. It seems probable that such can be taking place since there is a possibility of the effect of stray valence out from the aldehyde grouping which will influence an adjacent molecule and make for greater packing. Figures 8 and 10 show that in the low concentrations of these compounds there are small differences between the two and that only as the concentrations increase does glyoxylic acid give evidence of closer packing. This is in accord with the picture just given.

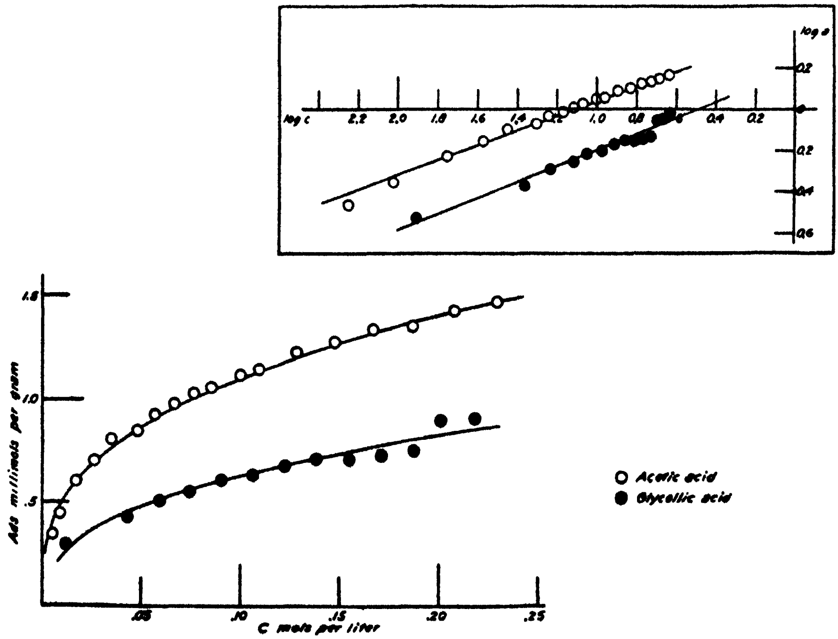

FIG. 11. ADSORPTION ISOTHERMALS SHOWING THE EFFECT OF THE HYDROXYL GROUP: ACETIC AND GLYCOLIC ACIDS

The graph on the lower left represents the plot arithmetically; on the upper right, logarithmically.

Two examples are given of the effect of the keto group on adsorption of acids. Pyruvic and levulinic acids are compared with propionic and valeric acids. Propionic acid at saturation has a relative area of 21 sq. A.U. and pyruvic acid 23.7 sq. A.U., while valeric and levulinic acids have areas of 21 and 30.4 sq. A.U., respectively. The position of the keto group evidently plays a rôle in the adsorption of these derivatives, for pyruvic acid derived from a shorter chain acid than levulinic acid has such a group on the α-carbon atom, while levulinic acid is a γ-keto acid. The keto group, apparently, has small influence when the molecule possesses a short hydrocarbon chain. Stray valence forces are apparently brought more decidedly into play when the keto group occupies a position considerably removed from the carboxyl, as is the case with levulinic acid. These influences may be between the oxygen of the keto group and that of the carboxyl group, so that at "close packing" a condition exists which is similar in character to the dicarboxylic acids. This is even more evident since the ratio between the relative areas of valeric and levulinic acids is the same as that for the mono- and di-carboxylic acids, i.e., 2:3. One may be tempted to say that these stray valences are of maximum influence between the oxygen atoms of the keto and carboxyl group within the molecule, since even at low concentrations the adsorption of levulinic acid is materially less than is that of valeric acid (figure 10).

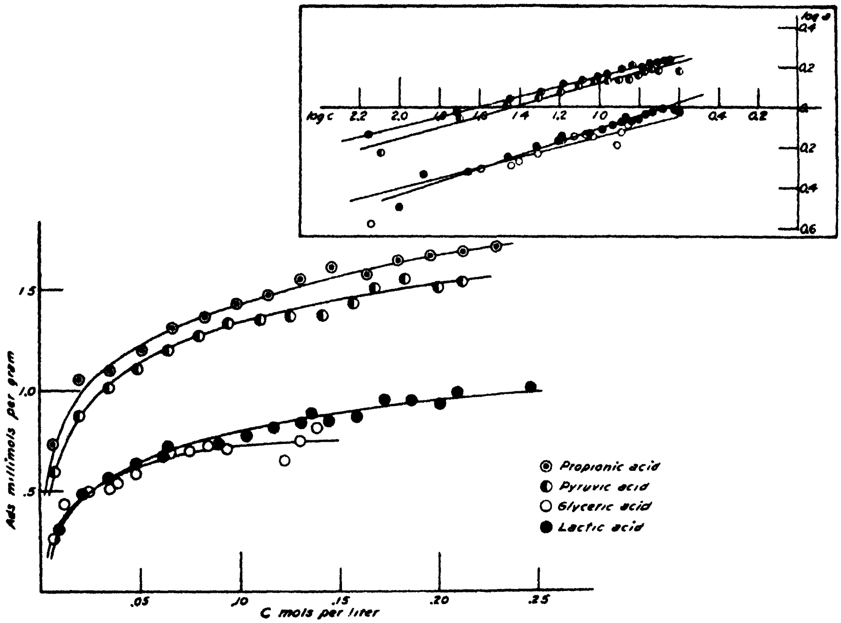

FIG. 12. ADSORPTION ISOTHERMALS FOR PROPIONIC ACID, ITS MONO- AND DI-HYDROXY DERIVATIVES AND ITS KETO DERIVATIVE

In the graph in the lower left of the figure values are plotted arithmetically; in the upper right, logarithmically.

The ratio between the saturated and unsaturated acids (i.e., succinic and its *cis*- and *trans*-isomers) is approximately 2:3. The average area given in table 11 is 30 sq. A.U. This value is about 6 per cent higher than the area obtained for the head group —CH = CHCOOH determined by other investigators, which value has a magnitude of 28.7 sq. A.U. (Rideal (37)). One can suppose in this case that at the packing of not only fumaric and maleic acids but mesaconic, citraconic, and itaconic acids as well, the head group determines the area of the molecule. All of the acids on the basis of our calculations have a relative area of fair constancy, so that it appears that the area of the —CH = CH—COOH group prevents any closer packing at the saturation point. Evidently the substitution of the methyl group for a hydrogen atom in the fumaric and maleic acid molecules makes an insignificant change in adsorption maxima and is no more a deciding factor in the quantity adsorbed than has been found in the case of the normal and iso acids discussed above.

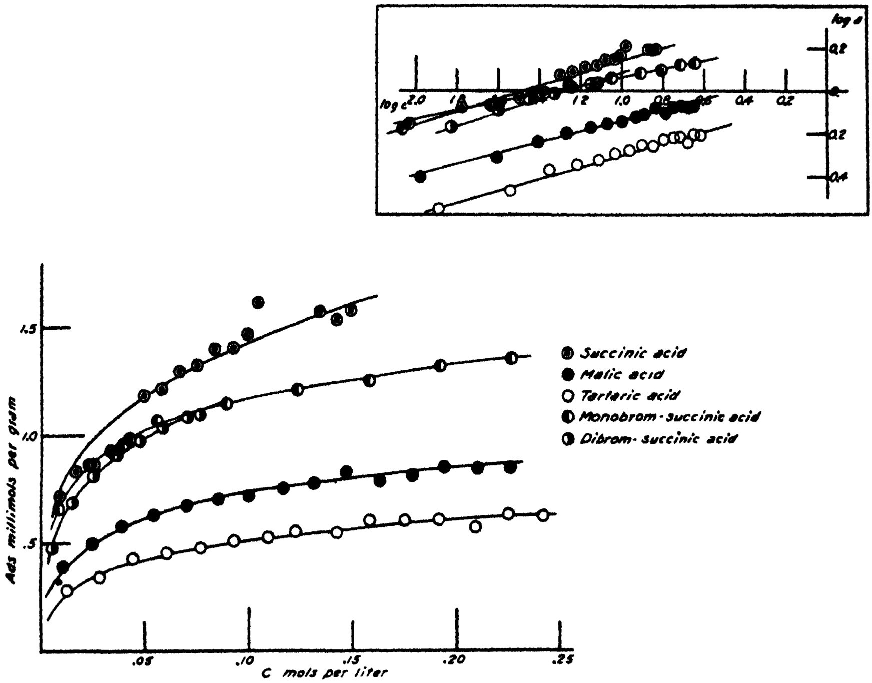

FIG. 13. ADSORPTION ISOTHERMALS COMPARING THE ADSORPTION OF THE MONO- AND DI-HYDROXY DERIVATIVES OF SUCCINIC ACID WITH THE MONO- AND DI-BROMO ACIDS

The curves in the lower left of the figure represent the values of C and a plotted arithmetically; those in the upper right the values plotted logarithmically.

V. SUMMARY

Adsorption studies have been carried out with a series of structurally related compounds on a single and comparable substrate. For this study a large sample of decolorizing carbon, Norite, was used. Members of the homologous series of fatty acids used were formic, acetic, propionic, butyric, valeric, caproic, and caprylic acids; members of the homologous series of dicarboxylic acids used were oxalic, malonic, succinic, glutaric, and adipic acids. To demonstrate the effect of various groupings in the molecules compounds were chosen and adsorption studies made as follows: for the grouped chain, isobutyric, isovaleric, and methylsuccinic acids; for the hydroxyl group, glycolic, lactic, glyceric, malic, and tartaric acids; for the carboxyl group, acids of the two homologous series listed above and citric acid; for aldehyde and keto groups, glyoxylic, pyruvic, and levulinic acids; for the double bond and variations due to *cis*-and *trans*-isomers, fumaric, maleic, mesaconic, itaconic, and citraconic acids; and for halogen substitutions mono-and di-bromosuccinic acids.

From these series of studies the following generalizations and conclusions are drawn:

1. The Freundlich adsorption isotherm is applicable to the data of these experiments and has been applied in calculating the areas under the curves for the various fatty acids. Ratios between the area under one isotherm between definite limits and that corresponding to the next higher member in the homologous series of fatty acids have been shown to have a better constancy than those obtained by the method suggested by Freundlich.
2. The Langmuir equation is applicable to these data.
3. Agreement has been shown between the β of Langmuir's equation (the maximum amount adsorbed when the equilibrium concentration is that of a saturated solution) and a obtained by substituting for C of the Langmuir equation the saturated concentration of the acid in question.
4. By a graphical method suggested by Polanyi and Heyne, and Polanyi and Goldman, the a at maximum C has been demonstrated to be of the general magnitude of β.
5. It is suggested that a more valid method for comparing the effect of molecular structure on adsorption is by comparison of the maximum value of the adsorbed, i.e., a when equilibrium concentration is that of a saturated solution.
6. Relative areas for the acids studied when a is a maximum have been calculated, based on definite assumptions, and by reference to these areas variations have been shown in adsorption due to the introduction of polar groups into the molecule.
7. The branched chain has little effect on the maximum adsorption of an acid.
8. As the number of carboxyl groups is increased the adsorption decreases greatly.
9. The introduction of the hydroxyl group has been shown to decrease markedly the total amount of acid adsorbed. A second hydroxyl group tends to decrease the adsorption to a still greater extent.

10. Adsorption is decreased by the introduction of the keto group into the molecule, the decrease being dependent on the length of the chain and the position of the polar group in the chain.

11. Glyoxylic acid is adsorbed to a greater extent than is acetic acid.

12. Little difference in total adsorption of *cis*- and *trans*-isomers has been demonstrated at maximum adsorption. The double bond, however, has been shown to have a decided tendency to decrease adsorption.

13. An alternation exists among the values of β (Langmuir's equation) for odd and even acids of the homologous series of both the mono- and di-carboxylic acids. Such alternation is characteristic of the solid state. This adds confirmation to the view that the lower members of the homologous series of the mono- and di-carboxylic acids are adsorbed in the solid state.

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A NEW INTERPRETATION OF THE ADSORPTION ISOTHERM

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To date, the most satisfactory theory which has been advanced to account for the relation of gas adsorption to pressure is that of Langmuir (1). This theory assumes that the time rate of condensation is proportional to the pressure and to the amount of surface remaining bare, and that the time rate of evaporation is proportional to the amount of gas adsorbed, which is in turn proportional to the amount of surface covered (assuming a monomolecular film). A mathematical equation is derived which is fairly simple for a surface made up of only one kind of elementary spaces, but becomes quite complex with an increase in the number of kinds of elementary spaces; so that, even for a surface comprising only two kinds of spaces, the evaluation of the constants in the mathematical equation becomes, in the words of Langmuir, "a somewhat laborious method of trial."

As Langmuir has pointed out, the above theory is not to be condemned simply because the equations are complicated. However, it is the purpose of this paper to propose a theory which is susceptible to a less complicated mathematical analysis and which, instead of requiring an intimate knowledge of the nature of the adsorbing surface in order to establish the mathematical function, will, if the theory be valid, give valuable information concerning the nature of the surface. This theory requires a slightly different picture of the kinetics of the adsorption process from that assumed by Langmuir.

Let us assume, as does the Langmuir theory in its simplest form, that the adsorbing surface may be divided into elementary spaces, each capable of holding one gas molecule. That is, an elementary space may be defined as a space whose attractive, or adsorbing, force is entirely satisfied by the adsorption of one gas molecule. Contrary to the Langmuir theory, however, instead of assuming that an actual *collision* between a gas molecule and such a space must take place entirely through the inherent kinetic energy of the molecule, let it be assumed that it is only necessary for the gas molecule, through its molecular motion, to come within a certain *radius of attraction* of one of the spaces. This seems to be a reasonable assumption, for, if a space on the surface has enough attractive force to hold a molecule after a collision, it surely can attract the molecule through a small distance. As soon as a gas molecule comes within this radius of attraction, it will be adsorbed and the attractive force will be temporarily satisfied. However, that will not prevent a second adsorbable gas molecule from coming within the required distance of the elementary space while the first is still held. As soon as the first molecule is released, the second will be adsorbed. At a given pressure, a certain fraction of the elementary spaces having a given adsorbing force will always have at least one gas molecule within their radii of attraction, which, on the basis of this theory, is tantamount to saying that at a given pressure a certain fraction of these spaces always have gas molecules adsorbed upon them.

From this point of view, the kinetic treatment proposed by Langmuir does not hold for the reason that the time rate of desorption, that is, the number of spaces actually becoming bare per unit time, is not independent of the pressure.

The chance for a given elementary space to be covered depends upon the chance of its having an adsorbable gas molecule within its radius of attraction. This is proportional to the pressure.

The theory may be developed mathematically in the following manner: Let the different kinds of elementary spaces on the adsorbing surface be classified merely on a basis of the pressures at which they become saturated, the saturation pressure of a given kind being defined as the lowest pressure at which there is always an adsorbable gas molecule within the range of attraction of every elementary space comprising that kind.

Let it be assumed that the amount of gas adsorbed upon each kind of spaces is proportional to the pressure and to the total number of spaces comprising that kind.

Let X = total amount of gas adsorbed at pressure P,
x_1 = amount adsorbed on first kind of elementary spaces,
x_2 = amount adsorbed on second kind of elementary spaces, and
x_n = amount adsorbed on n^{th} kind of elementary spaces.

Then, up to P_{n_s}, the pressure at which the n^{th} kind of space becomes saturated,

$$x_n = C_n A_n P \tag{1}$$

where C_n is a constant for the given kind of space, and A_n is the total number of spaces comprising the kind, and is constant for the given quantity of adsorbent. That is, CA is a parameter constant for a given kind and different for different kinds. It will be referred to as the coefficient of adsorption for the given kind of spaces.

Then, for the given kind of space, $\frac{dx_n}{dP}$ = constant, and

$$\frac{dX}{dP} = \frac{dx_1}{dP} + \frac{dx_2}{dP} + \cdots \frac{dx_n}{dP} \tag{2}$$

including all kinds of spaces not saturated at pressure P. However, $\frac{dX}{dP} \neq$ constant, but diminishes as the respective kinds of spaces become saturated.

It should be theoretically possible to express the total number of elementary spaces belonging to each kind as a function of the saturation pressure. However, that would require, in order to establish the mathematical equation, a knowledge of the value of the constant, C, for each kind. The values of C are different for different kinds of spaces, because the attractive forces are different; if the attractive forces were not different, all spaces would become saturated at the same pressure. In order to obviate the above difficulty, it is convenient to express CA, rather than A, as a function of the saturation pressure, that is, to let

$$CA = f(P) \tag{3}$$

We then have

$$\frac{dX}{dP} = \sum_{P}^{P_s} \frac{dx}{dP} = \sum_{P=P}^{P=P_s} CA = \int_P^{P_s} f(P) \tag{4}$$

and

$$dX = \int_P^{P_s} f(P)dP \tag{5}$$

where P_s is the pressure at which the entire surface becomes saturated. At any given pressure P, X, the total adsorption, is the sum of the amounts adsorbed on all kinds of spaces up to pressure P. Therefore

$$X = \int_0^P \int_P^{P_s} f(P)dPdP \tag{6}$$

As a matter of convenience in demonstrating the application of the theory, let it be hypothetically assumed that the distribution of the adsorption coefficients with regard to pressure follows the probability law (2). That is, let

$$CA = \frac{K}{\sqrt{\pi}} e^{-K^2P^2} \tag{7}$$

where the pressure is measured positively and negatively from the value corresponding to the maximum value of CA, or

$$CA = \frac{K}{\sqrt{\pi}} e^{-K^2(P-P_m)^2} \tag{8}$$

where the axes have been shifted to avoid negative values of P and P_m

is the new coördinate of the pressure corresponding to the maximum value of CA. Then

$$X = \int_0^P \int_P^{P_s} \frac{K}{\sqrt{\pi}} e^{-K^2(P-P_m)^2} \mathrm{d}P\mathrm{d}P \tag{9}$$

Since the probability equation may be integrated only by expanding into an infinite series and integrating each term separately, it is more convenient to integrate mechanically. Figure 1, curve 1, shows the distribution of CA with regard to saturation pressure when K in equation 9 is arbitrarily assigned a value of 0.5. Theoretically, of course, $P_m = \infty$.

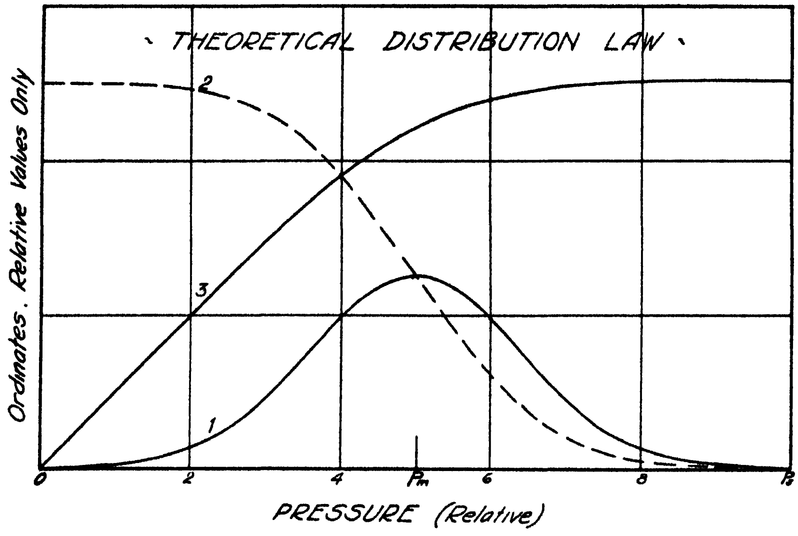

FIG. 1. HYPOTHETICAL CURVES

Curve 1, distribution of adsorption coefficients with respect to saturation pressures. Curve 2, $\frac{\mathrm{d}X}{\mathrm{d}P}$ versus P. Curve 3, adsorption isotherm, X versus P.

However, in the figure, the origin has been shifted to that pressure at which $CA = 0$ within the limitations of the scale.

Figure 1, curve 2, is obtained by plotting against pressure, P, the area under curve 1 from P to P_s, the pressure at which the entire surface becomes saturated. It represents the relation of $\frac{\mathrm{d}X}{\mathrm{d}P}$ to P. Figure 1, curve 3, is obtained by plotting the area under curve 2 from 0 to P. It represents the relation of X to P or, in other words, is the hypothetical adsorption isotherm. Only the central part of this curve resembles an actual isotherm curve, which means, of course, that the hypothetical assumption is not the correct one. By a method of trial, curve 1 doubtless could be altered in such a way as to make curve 3 more nearly resemble an isotherm curve. This is unnecessary, however, for it is more convenient to attack the problem in the following manner:

Since curve 2 is obtained by integrating curve 1 and curve 3 by integrating curve 2, in any actual case curve 2 may be obtained from curve 3 and curve 1 from curve 2 by the reverse process of differentiating. In other words, in figure 1 curve 3 represents X versus P, curve 2 represents $\frac{dX}{dP}$ versus P, and curve 1 represents $-\frac{d^2X}{dP^2}$ versus P, the minus sign being introduced on account of the fact that $\frac{dX}{dP}$ decreases as P increases.

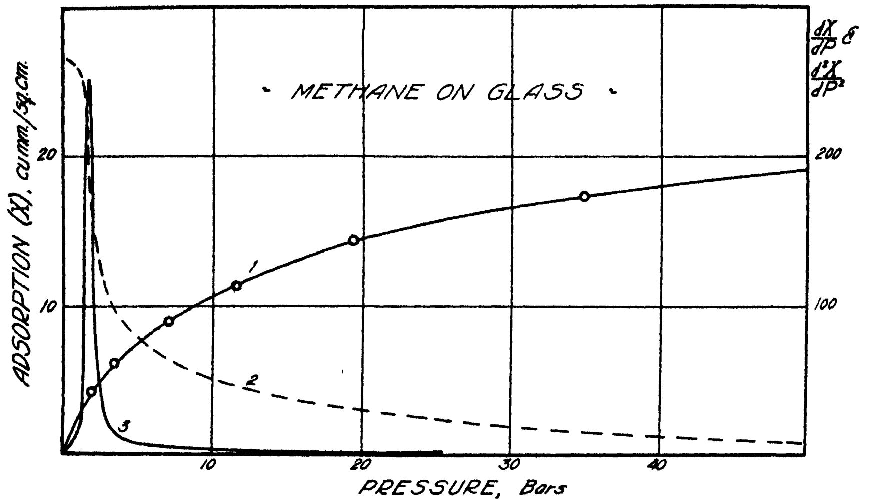

FIG. 2. ADSORPTION OF METHANE ON GLASS (LANGMUIR)

Curve 1, adsorption isotherm. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures.

Figure 2, curve 1, represents the isotherm for the adsorption of methane on glass, taken from the data of Langmuir (1). Figure 2, curve 2, represents $\frac{dX}{dP}$ versus P and figure 2, curve 3, represents $-\frac{d^2X}{dP^2}$ versus P, the differentiation being done mechanically in each case. This shows a maximum value of the adsorption coefficient (negative of second derivative) at a saturation pressure of approximately 1.7 bars, which means that there is a maximum amount of adsorption on spaces becoming saturated at that pressure. Since the curve is so steep on either side of that pressure, the glass surface may be regarded as composed of elementary spaces which are nearly all of the same kind.

Figure 3 represents a similar treatment of the data of Langmuir for the adsorption of methane on mica. There are two maxima in the $-\frac{d^2X}{dP^2}$ versus P curve, indicating two principal kinds of elementary spaces on the mica surface. The same conclusion was reached by Langmuir by his method of treatment.

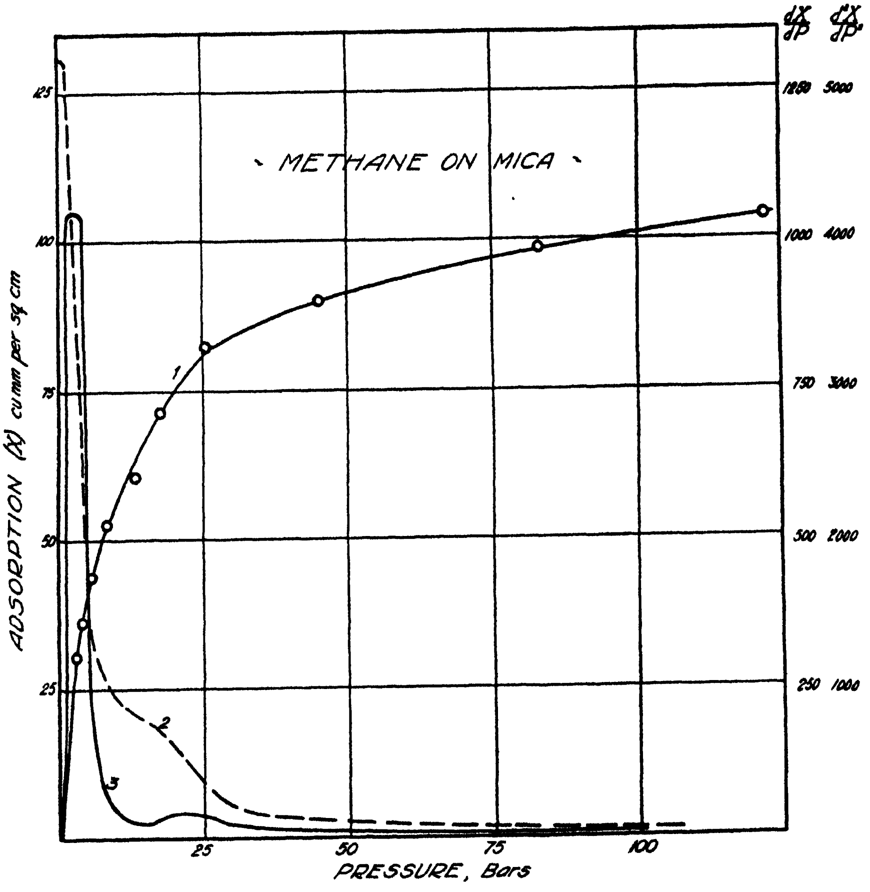

Fig. 3. Adsorption of Methane on Mica (Langmuir)

Curve 1, adsorption isotherm. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures.

Figure 4 represents a similar treatment of the data of Langmuir for the adsorption of nitrogen on mica. Curve 3 again shows two principal kinds of elementary spaces on the mica surface, whereas the Langmuir equation is satisfied by assuming only one kind. Since the mica specimens for the two experiments were prepared in exactly the same way, it is not unreasonable to expect similar adsorption phenomena for two inert gases.

If the theory proposed in this paper be correct, the CA–P distribution should be represented by the negative of the second derivative of any equation, theoretical or empirical, which absolutely satisfies the adsorption isotherm. The Langmuir equation applied to this case is of the form

$$X = \frac{abP}{1 + aP} \tag{10}$$

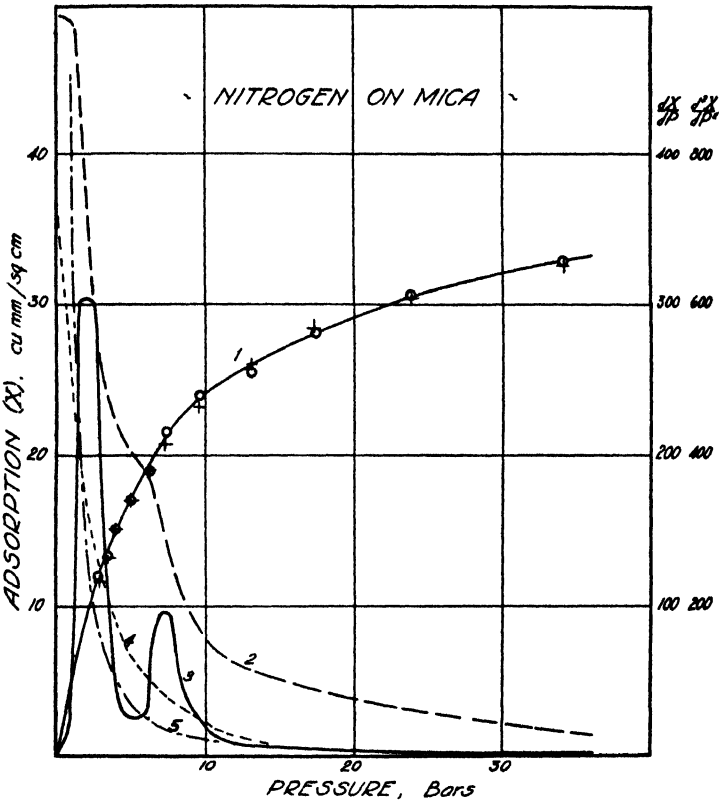

FIG. 4. ADSORPTION OF NITROGEN ON MICA (LANGMUIR)

Curve 1, adsorption isotherm: o, experimental values; +, Langmuir's calculated values. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures. Curve 4, negative second derivative of Langmuir equation versus P. Curve 5, negative second derivative of Freundlich equation versus P.

where a and b are constants for the given case, and the second derivative of this equation simplifies to

$$\frac{d^2X}{dP^2} = \frac{-2a^2b}{(1 + aP)^3} \tag{11}$$

whence

$$-\frac{d^2X}{dP^2} = \frac{2a^2b}{(1 + aP)^3} \tag{12}$$

The o's in figure 4, curve 1, represent experimental values, whereas the +'s represent the values calculated from equation 10 by letting $a = 0.156$ and $b = 38.9$, the values determined by Langmuir. Figure 4, curve 4, is obtained by plotting equation 12. By smoothing out curve 1 in accordance with equation 10, the inflection in curve 2 and the second maximum in the *CA* curve are lost entirely, and the first maximum in the *CA* curve is reached at $P = 0$. It is thus seen that in the case under discussion the equation used by Langmuir is reasonably applicable to the present theory only at pressures greater than approximately 10 bars. (Curve 4 practically coincides with curve 3 at pressures greater than 15 bars.)

Moreover, this discussion brings to light the fact that the Langmuir equation fails also to agree with the Langmuir theory in an important respect. One of the principal claims for the Langmuir equation is that it explains the fact that the adsorption is practically a linear function of pressure at low pressures. Without reference to the present theory of adsorption, it is a mathematical fact that the second derivative of a rectilinear equation is zero. The second derivative of the Langmuir equation not only is not approaching zero at low values of *P*, but its negative actually has its maximum value of $2a^2b$ at zero pressure. It therefore seems, when the equation is analyzed in this way, that it does not justify this claim made for it, which, however, probably has been amplified in text books, more than the originator intended.

On the other hand, the theory proposed in this paper is flexible in that respect, since the isotherm begins to bend downward at the pressure at which an appreciable number of elementary spaces become saturated, whether that pressure be zero or not. The accuracy of the interpretation in this and all other pressure ranges depends solely upon the accuracy of the experiments.

The limited applicability of the empirical Freundlich equation,

$$X = KP^n \tag{13}$$

may be represented as follows: From equation 13,

$$-\frac{d^2X}{dP^2} = \frac{Kn(1 - n)}{P^{(2-n)}} \tag{14}$$

Letting $K = 8.4$ and $n = 0.417$, the values assigned by Langmuir, and plotting equation 14 gives curve 5, figure 4. From this equation, the negative second derivative is infinitely large at zero pressure. A study of this curve indicates that by the proper evaluation of the constants the

Freundlich equation may be made to conform approximately to the facts only at pressures greater than that corresponding to the maximum value of the adsorption coefficient. This is a lower pressure in some cases than others, and therefore the empirical equation will apply over a wider pressure range in some cases than others. It will be most applicable in those cases in which a large number of elementary spaces become saturated at low pressures.

Further use of the data of Langmuir has not been made for the reason that in the other cases cited by him the number of experimental values given in the tables is not considered sufficient to warrant an assumption as to the exact shape of the isotherm curve. The data chosen were believed to be the most accurate available, and it is believed that the present theory explains them better than does the Langmuir theory.

The opportunity has not been available for a search for suitable data in other sources and the author therefore invites other workers dealing with adsorption isotherms to plot the negative second derivatives of those curves and criticise the theory accordingly. The treatment given in this paper is not regarded by the author as a finished product, but is offered in the hope that it may prove to be the nucleus of extended work in the field.

SUMMARY

A new theory of the kinetics of gas adsorption has been proposed.

It is assumed that, in order to be adsorbed, a gas molecule must only come within a certain range of attraction of the adsorbing surface, rather than actually collide with the surface through its molecular motion.

The amount of gas adsorbed upon a given kind of elementary surface space is proportional to the pressure.

Different kinds of elementary spaces become saturated at different pressures.

A mathematical treatment has been derived which is in better agreement with published data than is the Langmuir equation.

The applicability of the Langmuir equation to the present theory has been discussed and a discrepancy between the Langmuir equation and the Langmuir theory has been pointed out.

The applicability of the empirical Freundlich equation to the present theory has been briefly discussed.

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THE RELATION BETWEEN HEAT CONDUCTIVITY AND STRUCTURE IN SILICA AEROGEL

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The structural units of jellies have dimensions of such an order that they have failed to yield to the ordinary methods of mensuration. Electrical conductivity, diffusion, and adsorption measurements have yielded figures of questionable accuracy on account of the uncertainties involved in the interpretation of the results. Ultramicroscopic studies in optically empty jellies are fruitless, while a measurement of the Rayleigh scattering of light, when it is intense enough to be measured, can at best give only qualitative results because the elements of structure are far too close together to obey Rayleigh's equations. The situation is somewhat better with gelatinous membranes where ultrafiltration of colloidal particles and Bechold's bubble test are available, but in the former case one is far from certain that the maximum diameter of particle that passes the membrane is within a factor of 10 of the actual average diameter of channel through which it passes, and a corresponding uncertainty enshrouds the bubble test, owing to the fact that only the largest passages can be thus estimated and also owing to uncertainty of the surface tension at small radii of curvature. X-ray methods can indicate only the size of crystal in crystalline gels, but can in no way indicate the relation between size of crystal and size of structural units, e.g., fibrils, platelets, spheres, etc., from which the gel is constructed.

The development of a process for the replacement of the liquid in a jelly by a gas with little or no change in its structure (2) has made available a powerful new measuring rod, the mean free path of the gas molecules. The kinetic theory of gases has received such substantiation and acceptance in the past two-thirds of a century that the mean free path may be regarded as one of the well-established physical quantities.

Two methods of associating dimensions within the aerogel with the mean free path of a gas have been used in this laboratory. By forcing a gas through an aerogel at different absolute pressures, the pressure at which the type of flow through the gel changes from viscous to molecular can be found and related to the average size of opening through which the gas passes. The results of this work will be published later. The second method relies upon the linear relation between heat conductivity of a gas and its mean free path, other quantities being held constant.

RELATION BETWEEN MEAN FREE PATH AND HEAT CONDUCTIVITY OF A GAS

According to the kinetic theory of gases, thermal conductivity of a gas is associated with the mean free path by the equations

$$k = Bc_v\eta \tag{1}$$

and

$$\eta = 0.35\ \rho v l \tag{2}$$

where k is the coefficient of heat conductivity, B is a constant, c_v is the specific heat of the gas at constant volume, η is the viscosity, ρ the density, v the arithmetical average velocity of the molecules, and l the mean free path. The constant 0.35 is due to Boltzmann. The coefficient k can then be represented by the expression

$$k = k'l \tag{3}$$

where k' is a function of the pressure, temperature, and composition of the gas.

Since we know nothing of the nature of the fine structure in an aerogel except that the free spaces are much larger than the elements of structure themselves (aerogels with 98 per cent void space have been produced), we will think of a large number, N, of molecules randomly distributed through the aerogel, starting from rest and moving in straight lines in all directions until they collide with structural elements of the gel. If the structure is random, which we must assume, the fraction $\frac{dn}{N - n}$ of the molecules that have not yet struck surfaces will impinge within the distance dx, where n is the number that have already struck. Therefore

$$dn = \frac{N - n}{L}\,dx \tag{4}$$

where $\frac{1}{L}$ is the proportionality factor. Integration gives

$$n = N\left(1 - e^{-\frac{x}{L}}\right)$$

which is the familiar equation connecting the number of impacts between molecules with distance in a gas, and L can now be defined as the mean free path of a highly attenuated gas within the aerogel. In other words, $\frac{e - 1}{e}$ or 63 per cent of the molecules will hit surfaces in the distance L.

In the same manner one finds that when the pressure is sufficiently high many molecules strike others in going between surfaces,

$$dn = \left(\frac{N - n}{L} + \frac{N - n}{l}\right) dx = \frac{(N - n)(l + L)}{Ll} dx$$

and the mean free path of the gas in the aerogel is

$$l_a = \frac{Ll}{L + l} \tag{5}$$

Now substituting equation 5 into equation 3

$$k_a = k'l_a = k' \frac{lL}{L + l} = k \frac{L}{L + l} \tag{6}$$

where k_a is the conductivity coefficient for the gas while in the aerogel. It was in this approximate form that the equation was used in a former publication (3).

More careful consideration of the mechanism of heat transfer through an aerogel indicates that the coefficient B in equation 1 should be different for the gas in the aerogel than for the free gas under the usual measuring conditions where the mean free path is very small with respect to the distance apart of the calorimeter plates. Where the molecules are moving in straight lines between surfaces with only occasional impacts in between, as is the case within aerogels at low pressures, it is readily shown that

$$k = \frac{Mc_vIl}{6.06 \times 10^{23}}$$

where M is the molecular weight and I is the number of impacts of molecules on unit area in 1 sec. Measuring length in centimeters and pressure in millimeters of mercury,

$$I = 1.99 \times 10^{16} \frac{P}{\sqrt{MT}}$$

which yields

$$k_a = 0.058 \sqrt{\frac{M}{T}}\, C_v l_0 \frac{L}{L + \frac{l_0}{p}} \tag{7}$$

where l_0 is the normal mean free path of the gas at the given temperature and a pressure of 1 mm.

Equation 7 assumes that with every impact a molecule comes to thermal equilibrium with the surface on which it strikes before it departs. If one assumes that only the fraction a of the molecules comes to thermal equilibrium and that the fraction $1 - a$ is specularly reflected, the equation becomes

$$k_a = 0.058\, a \sqrt{\frac{M}{T}}\, c_v l_0 \frac{L^2}{\dfrac{2Ll_0\,(1 - a)}{p} + aL\left(L + \dfrac{l_0}{p}\right)} \tag{8}$$

Equations 7 and 8 neglect the correction factor proposed by Chapman (1) as being inoperative under these conditions.

EXPERIMENTAL PROCEDURE AND RESULTS

The calorimeter and method of operation were described in a former paper (3).

The gel was made by mixing E Brand water glass, kindly furnished by the Philadelphia Quartz Company, diluted to a specific gravity of 1.20, with an equal volume of 4.3 N acetic acid and casting over mercury in paraffined crystallizing dishes. After 48 hours the cakes were removed, washed free of salts, and extracted in a Soxhlet extractor with 95 per cent alcohol until the water content of the cakes was less than 10 per cent. They were then placed in an autoclave with excess alcohol and heated to 260°C., at which temperature the alcohol was allowed to escape. The cakes of very nearly the same thickness were next trimmed with a sharp knife to shapes that could be fitted closely together on the lower plate of the calorimeter. The calorimeter was then assembled and evacuated to less than 0.01 mm. for half an hour in order to remove adsorbed moisture.

Following the evacuation the gas to be used was admitted and measurements made at pressures differing from each other roughly by a factor of 2. The lowest pressure used was generally in the neighborhood of 10 mm. to avoid making measurements at pressures so low that the conductivity of gas films between the pieces of silica aerogel and the calorimeter plates would be affected.

As was pointed out in the earlier publication in which measurements were reported on powdered aerogel, reproducibility of results is good. Only occasionally does a reading in a series fall far from a smooth curve, and those occasions have been traced to a drift of the zero point on the high sensitivity galvanometer that controls the temperature of the guard ring.

The results of the measurements with three gases, air, carbon dioxide, and dichlorodifluoromethane, are presented in table 2 and the figure. These three gases were chosen since they represent three very distinct types and possess mean free paths, as calculated by equation 2, differing by a factor of 3. Measurements were also made with hydrogen, but were not satisfactory on account of the high thermal conductivity between guard ring and disc and the consequent uncertainty of readings due to the unusually bad zero point drift of the galvanometer. When the galvanometer suspension has been replaced, this series will be repeated and the results reported later.

Table 1 gives the calculated constants required in equation 7 for the three gases. The required data were obtained from the International Critical Tables except for the last gas, for which the data were obtained from the literature (4) and from Mr. A. L. Henne. The average temperature of measurement was 33.3°C. Conductivities are reported as $\frac{\text{cal.}}{\text{cm.} \times \text{sec.} \times {}^\circ\text{C.}}$ To demonstrate the reproducibility of the data, two series of measurements were taken on air and distinguished in the figure by crosses and circles.

TABLE 1

Calculated constants for air, carbon dioxide, and dichlorodifluoromethane

GAS	l_0	$0.058\sqrt{\frac{M}{T}}c_v l_0$
Air	7.46×10^{-3}	2.27×10^{-5}
CO_2	5.04×10^{-3}	1.67×10^{-5}
CCl_2F_2	2.46×10^{-3}	1.20×10^{-5}

TABLE 2

Observed conductivity of silica aerogel

AIR		CO_2		CCl_2F_2	
P	Conductivity $\times 10^5$	P	Conductivity $\times 10^5$	P	Conductivity $\times 10^5$
mm.		*mm.*		*mm.*	
740	4.85*	745	4.33*	740	3.71*
363	4.16	397	3.84	406	3.38
183	3.63*	206	3.42	259	3.18
2	2.93	100	3.06*	123	2.86*
43	3.10	49	2.98	59	2.63
94	3.26	24	2.80	29	2.59
206	3.61	9	2.65	8	2.68
387	4.06				
743	4.83				

* Values used in calculating the results given in table 3.

CALCULATIONS

Owing to the difficulty of obtaining good thermal contact between the calorimeter plates and the cakes of aerogel, there is a constant thermal resistance in series with that of the aerogel itself. The series conductivity will be called k_2. Also in parallel with the conductivity due to the gas in the aerogel, there is a constant conductivity, k_3, due to the continuous structure of silica and to the gas in the small spaces between the cakes. The overall conductivity, k, as measured in the calorimeter, is related to the other conductivities by the equation

$$\frac{1}{k_g + k_3} + \frac{1}{k_2} = \frac{1}{K} \tag{9}$$

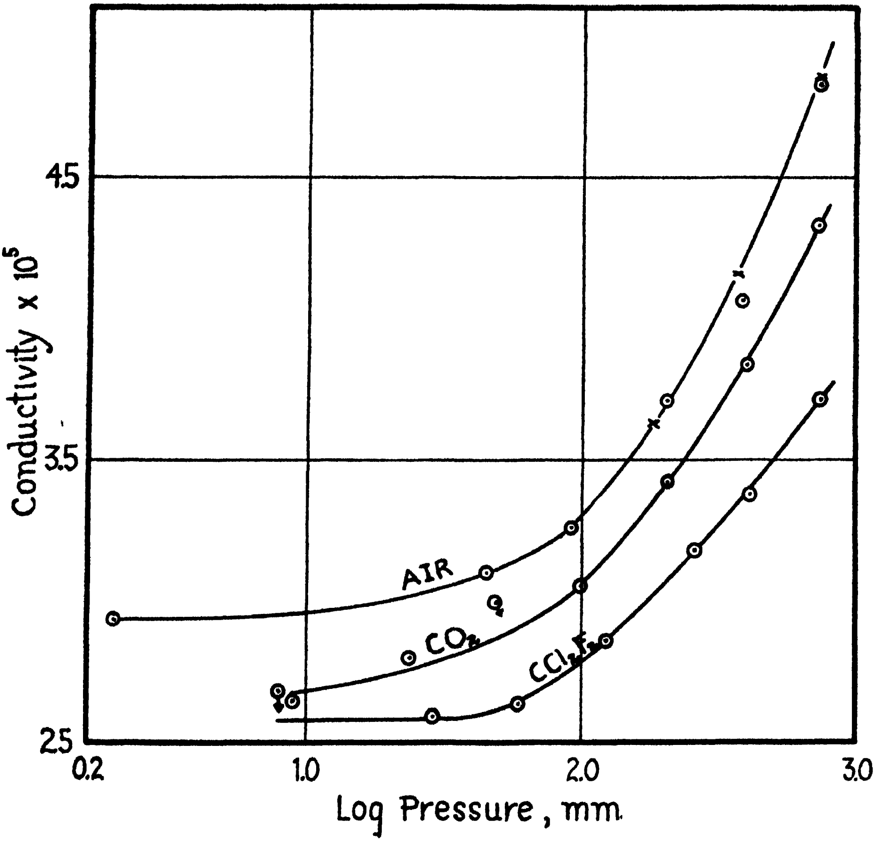

FIG. 1. CONDUCTIVITY OF SILICA AEROGEL

To be perfectly general it is evident that equation 8 should be used for k_g in order to allow for a possible accommodation coefficient a less than 1. From what is known of a gel surface, however, it seems permissible, at least as a first approximation, to establish $a = 1$ and therefore gain the decided advantage of the simplicity of equation 7.

From the curves in the figure, one can estimate the value of k_3 for each gas as the asymptotic value at low pressures. This quantity combined with the calorimetric conductivities at two other pressures enables one to solve equation 7 for L. Table 3 gives the results of such calculations, using the values of K starred in table 2.

It is gratifying that by the use of three such different gases one should obtain such concordant results, and it gives one confidence both in the method and in the verity of the conclusions. The average distance apart of the structural elements in this batch of silica aerogel whose apparent density was 0.184 g. per cubic centimeter must lie very close to 5×10^{-6} cm., or 500 A.U.

There is one second-order source of error in these calculations that must eventually be mathematically evaluated. In the derivation of the coefficient 0.058 in equation 7, it was assumed that all of the impacts experienced by gas molecules within the aerogel are with surfaces. This assumption is a very close approximation, particularly at the lower pressures, but at the higher pressures, where there are more direct impacts between gas molecules, the coefficient should increase slightly. This dependence of the coefficient upon pressure will slightly increase the calculated value of L. Nevertheless, as a first approximation and as a very acceptable value until this function can be evaluated, the average of table 3 can stand.

TABLE 3

Calculated free spaces within the aerogel

GAS	k_3	L
		cm.
Air	2.9×10^{-5}	4.8×10^{-6}
CO_2	2.6×10^{-5}	5.1×10^{-6}
CCl_2F_2	2.5×10^{-5}	5.1×10^{-6}
Average		5.0×10^{-6}

SUMMARY

The heat conductivity of silica aerogel of density 0.184 filled with three different gases at various pressures has been measured. The relation between heat conductivity, mean free path of the gas molecules, and the average distance separating the elements of structure in the aerogel has been derived from kinetic theory, and the last quantity has been evaluated at 5.0×10^{-6} cm.

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MOLECULAR DIFFUSION INTO WOOD[1]

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I. STATEMENT OF PROBLEM

One of the purposes of the study of molecular diffusion into a gel has been to obtain information about the structure of the gel. Thus, in spite of the fact that early investigators had assumed the gel to have no effect on the diffusion, it is now a matter of record that mechanical blocking, wall friction, and viscosity effects do modify the rate at which a simple solute molecule can diffuse across an interface and into such a solid. It appeared possible to us that the methods which have been successful in the study of gels could be extended to the porous solids. Therefore it was decided to measure the rate of diffusion, from dilute aqueous solutions, of the neutral molecules urea, glycerol, and lactose into wood samples, with the expectation that these diffusion data could be used to estimate the effective mechanical blocking. Wood samples were chosen because through the efforts of the scientists at the U. S. Forest Products Laboratory and elsewhere the capillary dimensions for certain species are quite accurately known. This report describes the results obtained in a somewhat extended series of experiments and discusses their significance.

A number of interesting experiments have followed the successful analyses by March and Weaver (8) and by Langer (7) of the mathematical problem involved in a diffusion experiment in which the process is allowed to take place across the interface formed by a stirred liquid in contact with a gel or porous solid. As a result of experiments based upon this analysis Friedman and Kraemer (3) have been able to make observations of the diffusion of non-electrolytes into gelatin gels, Friedman (2) and Klemm and Friedman (4) have been able to extend the work to agar and cellulose acetate gels, and Wolkowa (14) has obtained data for the diffusion of glucose into silica gels. In all these cases the diffusion into the gel is slower than it is into pure water at the same temperature. Friedman and Kraemer considered three causes for the retarded diffusion: a mechanical blocking by the gel substance, an additional resistance due to the proximity of the diffusing molecule to the capillary walls, and an increased viscosity of the dispersion medium due to the solution in it of a certain amount of the gel substance. Correction for these effects was made by the use of an equation of the form,

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[1] A more complete account of this work is to be found in the thesis of L. C. Cady, presented to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy and filed in the Library of the University of Wisconsin in August, 1934.

$$D_w = D_s\,(1 + \pi)\,(1 + 2.4\,r/R)\,(1 + \alpha) \tag{1}$$

In this equation,

D_w is the diffusion coefficient of the substance into water,

D_s is the diffusion coefficient of the substance into the gel or porous solid,

π is the correction factor for mechanical blocking,

r is the radius of the diffusing molecule,

R is the radius of the pore through which the diffusion is taking place, and

α is the correction factor for changed viscosity.

In the treatment of our experimental data we shall prefer to make use of another equation, as follows:

$$D_w\,(1 - \pi) = D_w \cdot A = D_s\,(1 + 2.4\,r/R)\,(1 + \alpha) \tag{2}$$

Our work has been done with wood samples, and R is now to be interpreted as the effective radius of the pit membrane pores. Since mechanical blocking serves to reduce the unit area through which the diffusion can take place, it has seemed logical to compare D_s and D_w for a process taking place across equal areas. This necessitates the adjustment of D_w to the reduced open cross-sectional area of the porous substance. Thus, the mechanical blocking may be taken into account by multiplying D_w by a factor A, which is the fraction of the area unobstructed by the solid substance. Then differences between D_w values which have been adjusted in this way for reduced cross-sectional area and D_s are due to other factors, including the anisotropic character of the wood.

Aside from microscopic measurements with extremely thin sections there is no direct method by which the amount of open area in a given surface can be evaluated. The method of attack most frequently used is based upon a determination of the partial pore volume of a sample, using density measurements. If the partial pore volume is represented by S, then $S = 1 - g/d$. In this definition, g is the weight of the gel or porous solid per cubic centimeter, and d is the density of the solid material forming the structure.

Thus, the problem becomes one of expressing the factor A in terms of S. There are two conditions which any equation relating A and S should fulfil. When the partial pore volume is zero the substance is solid throughout, the area is completely blocked, and the factor A becomes zero. Likewise, when the partial pore volume is unity there is no mechanical blocking, none of the area is obstructed, and A becomes unity. The mechanical blocking factor has been obtained in different ways by interested investigators. In order to collect in one place a few of the results, table 1 and figure 1 have been prepared.

Buckingham's equation was based upon his observations of the resistance experienced by carbon dioxide and oxygen diffusing through soil. The Dumanski expression resulted from an attempt to calculate by theory the area in a single plane of the sections of spherical molecules forming the disperse phase. It was applied by Dumanski to the correction of both electrical conductivity and diffusion data for gels. To correct conductivity data which were obtained with samples of wood, Stamm modified the equation, because in this case the structural units are elongated rather than spherical in shape. The diffusion problem was not considered by the latter investigator.

TABLE 1

Evaluation of mechanical blocking factor A

VALUE OF A	INVESTIGATOR	REFERENCE
S^2	Buckingham	U. S. Department of Agriculture, Bur. Soils, Bulletin No. 25 (1904)
$1 - (1 - S)^{2/3}$	Dumanski	Kolloid-Z. **3**, 210 (1908)
S	Stamm	J. Phys. Chem. **36**, 312 (1932)

Since Friedman and his associates have adopted the Dumanski relationship for their work it may be remarked that their use of equation 1 is equivalent to a definition of the mechanical blocking factor such that,

$$A = \frac{1}{1 + (1 - S)^{2/3}}$$

This equation does not meet the condition that A must be zero when the partial pore volume is zero, therefore it cannot have any general validity. The reason why its use with gel systems which have very large values of partial pore volume has not led to apparent difficulties is evident from an inspection of figure 1.

The correction to be made for the increased frictional resistance to the movement of a molecule in the neighborhood of a wall has been studied at some length by Ladenburg (6), Arnold (1), and many others. The correction used in the diffusion equations (1, 2) is that of Ladenburg. The effect of the proximity of the wall surface on spheres falling in cylindrical glass vessels was measured, and Stokes' law of fall was modified to take it into account. Arnold confirmed the Ladenburg correction and showed that it is independent of the viscosity of the liquid in which the molecule or particle is moving.

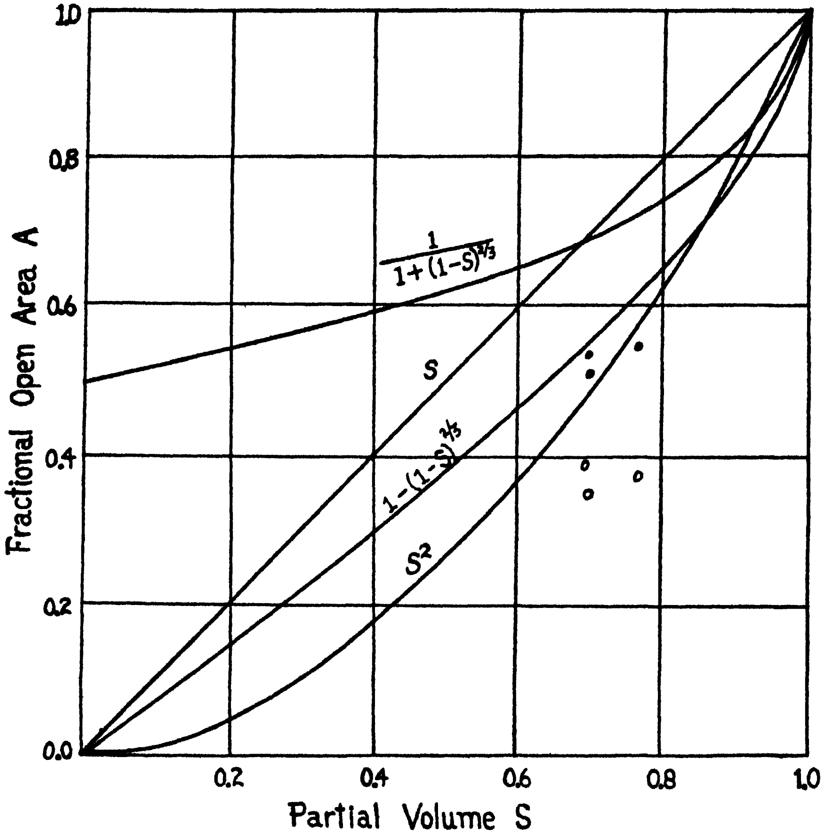

FIG. 1. EVALUATION OF MECHANICAL BLOCKING FACTOR

In order to correct the law of Stokes the viscosity was multiplied by the factors $(1 + 2.4\ r/R)$ and $(1 + 3.3\ r/h)$. In these factors h is the length of the capillary, and r and R have the significance already assigned them. The second factor becomes appreciable in the case of short tubes with closed ends and may be disregarded in the gel and wood problems. For wood, h would be twice the diameter of a lumen which is about one thousand times the value of r.

Obviously the additional resistance to motion caused by the proximity of the wall will manifest itself for a limited range of values of r/R. When

r/R is large, one is dealing with a condition approaching ultrafiltration, but when r/R is very small, the wall is so far removed that the condition is one of free fall, or in the case of a diffusion, one of free diffusion. The data of Ladenburg indicate that this ratio should have values between 1/90 and 1/11 if the first factor is to be applicable without modification. Arnold's curves place the lower limit in the neighborhood of 1/100, with the upper limit at about 1/10.

The correction factor α for increased viscosity of dispersion medium is obtained from the difference between D_s at zero concentration of solid and D_w. Since there is only one "concentration" of wood substance when the voids or capillaries are filled with water, it is not possible to estimate α by an extrapolation of the kind resorted to when synthetic gels are being considered. For reasons which cannot be given at this time it seems reasonable to conclude that the factor α can be considered to be negligible in our work with wood sections.

If this correction factor for increased viscosity of medium can be neglected, diffusion experiments of the type to be reported here can give considerable information with regard to the magnitude of the mechanical blocking effects, because the radii of the diffusing molecules and the average radii of the pores of the pit membranes are known with some degree of accuracy. Stamm (13) has summarized the results for R obtained by using several independent methods. In this way it should be possible to differentiate between the several equations proposed to calculate the magnitude of the mechanical blocking coefficient. In addition, differences between observed values and values obtained by calculation with the equation adjudged to be most nearly correct can be ascribed to the anisotropic character of the capillary spaces and to the presence of lumen pores without outlet.

It might be assumed that diffusion studies of the kind we are to report would make possible an estimate of an average radius of the pit membrane pores in wood sections, but when it is realized that the principal cause of the reduction of diffusion is the mechanical blocking, the difficulties involved become apparent. We have little exact information about several factors which determine the effective area available for the diffusion. Furthermore, since the effects due to mechanical blocking are very large compared to those which result from the additional frictional resistance to motion due to the proximity of the walls, small errors in the A factor would lead to large errors in the determination of the ratio r/R, and therefore in the effective capillary area of the pores of the pit membranes.

II. MATHEMATICAL FORMULATION AND EXPERIMENTAL PROCEDURE

The coefficient of diffusion or diffusion constant is defined as the quantity of matter which in unit time moves through a unit of cross section under unit concentration gradient. In this work it was required to determine the constant for various solute molecules, moving across the interface formed by the stirred solution in contact with a wood section, from observations of the decrease in concentration of the solution with time. March and Weaver showed that the diffusion constant, D_s, of a solute moving into the solution contained in a porous solid is given by the expression

$$D_s = \frac{a^2T}{t} \tag{3}$$

In this equation D_s is the diffusion constant expressed in cm.^{2} per second, and a is the thickness of the solid and also the depth of the solution above the solid. The value of T is found from the equation,

$$V = \frac{1}{2} - (0.327e^{-4.117T} + 0.0766e^{-24.14T} + 0.0306e^{-63.68T} + 0.0160e^{-123T} + 0.0100e^{-200T} + 0.0067e^{-299T} + \cdots)$$

In this expression V is the fraction of the total amount of solute which has diffused into the void spaces of the solid. In our experiments this quantity was found by determining the concentration of the solution above the block of wood with an immersion refractometer. At any time, t,

$$V = \frac{R_0 - R_t}{R_0 - R_w} \tag{4}$$

Here R_0 is the reading of the refractometer for the solution at time, $t = 0$,
R_t is the reading at time t, and
R_w is the reading for the solution originally filling the void spaces of the solid.

In order that equation 3 be exact it is required that the depth of solution and thickness of the solid be the same, and that the solution be maintained at uniform concentration throughout. In order to use equation 4 in the form given, it is necessary to assume the concentration of solute to be directly proportional to the refractive index of the solution.

In practice, values of T were assumed and the corresponding values of V were calculated. A plot of V versus T was then made and values of T for any experimentally determined value of V were read from the curve.

In an experiment a block of wood was saturated with water and fitted into a thermostated brass diffusion chamber. The solution containing nearly spherical solute molecules was placed in contact with the block, and the change of concentration with time, as the solute diffused into the block of wood, was observed.

Samples of cedar and white fir were obtained from freshly felled trees about 15 in. in diameter. The sample of white pine was a kiln-dried piece, and results with it were obtained largely while developing the technique of the method. The Western hemlock sample was furnished by the U. S. Forest Products Laboratory. Sections taken from these were numbered

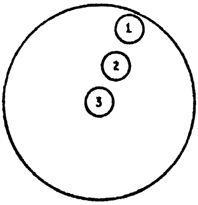

FIG. 2. LOCATION OF SAMPLES TAKEN FROM TREE

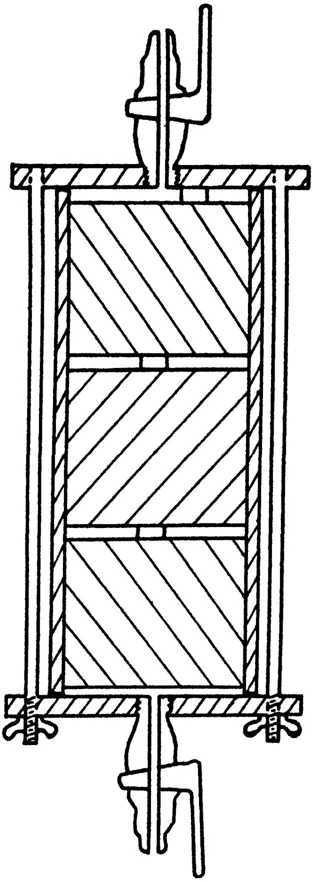

FIG. 3. EVACUATION CELL

as shown in figure 2. All samples were turned to the required size in a lathe and the ends were coated with paraffin to prevent drying and checking. To lower the humidity to a sufficient extent to avoid growth of molds, the samples were kept over a saturated solution of barium chloride.

The turned wood samples were cut into cylindrical blocks of the desired length, which varied from 1.5 to 4.0 cm. The exact thickness was measured with a micrometer caliper. The samples were placed in an evacuation cell whose construction is indicated by figure 3. This cell was a brass cylinder 5 in. long and 2 in. in diameter. Cover and bottom, provided with brass stopcocks, were arranged so that they could be clamped to the cylinder. The upper stopcock was connected to a vacuum pump and the lower one was attached to a mercury manometer. Rubber gaskets between the cylinder and the cover and bottom sealed the apparatus. The cylinder, with block in place, was maintained for about twenty-four hours at a pressure of 4 to 5 mm. of mercury. Water was introduced through the lower stopcock of the cell in order to fill the evacuated void spaces in

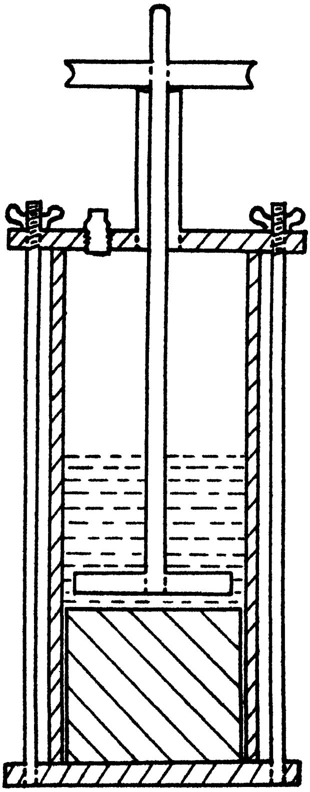

FIG. 4. DIFFUSION CELL

the block of wood. The sample was then kept for four weeks or longer in a vacuum desiccator filled with water, from which the air was exhausted at intervals.

The diffusion apparatus proper is shown in figure 4. It resembled the evacuation cell in form except that it had no stopcocks and the cover piece was provided with a stirrer and tapped hole to permit removal of the sample.

Since diffusion was to take place only across the upper surface of the block, it was necessary to make it impossible for the solution to come into contact with the sides and bottom of the block. This was accomplished by painting the block on these faces with an aluminum–glyptal paint, and then coating them with a layer of paraffin to such a thickness that the block would not quite slip into the cylinder. The cylinder was then warmed and the paraffined block forced into it. On cooling, the block was firmly imbedded in the paraffin. The apparatus was tested for tightness by allowing it to stand full of water overnight. Any seepage of water along the sides of the block could be detected in this way. After inversion to remove the excess water, the cell was clamped firmly to a brass frame by means of which it was possible to lower the cell in fixed position into the thermostat. The temperature chosen for the experiments was 25°C. To start an experiment an amount of the solution, such that its height in the cell was equal to the height of the wood block, was introduced into the diffusion cell.

The choice of solute molecule was restricted for several reasons. The molecule should be nearly spherical in shape and of such radius that the ratio r/R falls within the limits mentioned in the previous section. The refractive index of the aqueous solution should be such that it varies linearly with the concentration of the solute. The solution should not cause change in any of the constituents of the wood. The molecules urea, lactose, and glycerol met these requirements fairly well. The concentration of the glycerol solution used was 4 per cent, while that of the urea and lactose was 5 per cent, by weight. The concentrations were kept as low as possible in order to avoid a "solute hindered" diffusion, but at the same time the concentration was great enough to allow a difference of reading of 15 to 20 immersion refractometer units between the solution and water at the beginning of the experiment.

Refractometer readings were taken at the beginning of the experiment and at intervals of from twelve to twenty-four hours. The diffusion was allowed to continue until successive readings indicated that equilibrium had been reached. Six to twelve values of the diffusion constant were determined for each block. In this way it was possible to obtain a representative value provided the variations between individual figures were not excessive. Preliminary experiments showed that there was no change of refractometer reading due to leakage, seepage, oil from the stirrer, or solution of material from the cylinder or paraffin. Further, no measurable sorption of solute by the wood substance was found. Before the start of all experiments the blocks were saturated as nearly as could be determined by weighing at intervals to constant weight. The rate of stirring was so adjusted that the solution was kept at uniform concentration without producing a vortex effect above the block. A stirrer speed of 275 R.P.M. was maintained.

The initial refractive index of the water saturating the block depended upon the amount of material extracted from the block and varied with the species of wood. It was assumed that the solution filling the void spaces of the wood and the solution covering the block had reached equilibrium during the time that the block was in the vacuum desiccator. The refractometer reading, R_w, was taken as the value obtained for the solution in which the block was saturated.

III. EXPERIMENTAL RESULTS

Data obtained in a typical diffusion measurement are presented in table 2. The values of D_s in this table check each other unusually well, but in practically all cases the mean deviation from the average value is less than 0.01.

The length of the block which could be used was fixed within definite limits by the dimensions of the diffusion cell, the amount of solution that could be stirred adequately, and the effect of sample removal upon the concentration of the remaining solution. It is evident from table 3 that the length of the block may be changed by 100 per cent without changing the diffusion coefficient to an appreciable extent.

Additional experiments were made in which the wood was saturated with the solution so that a diffusion of the solute into water above the block took place. When glycerol diffused into the seasoned heartwood of white pine a value of $D_s = 0.66 \times 10^{-5}$ was obtained. Reversing the experiment with glycerol diffusing into the water above the block the value $D_s = 0.63 \times 10^{-5}$ resulted. However, experiments in which the solute diffused out of the block into the water above it offered several difficulties and were not generally used.

When the pore dimensions of the wood blocks were larger, the values for the diffusion constants increased. In all, there could be distinguished: (1) hindered diffusion, in which the ratio r/R was not too small to be of significance; (2) free diffusion, in which the effective pores were small enough to prevent mixing of the water in the block with the solution, but large enough to allow *practically* unrestricted diffusion of the solute molecules; and (3) stirred diffusion, in which the pores were so large that mechanical mixing with the liquid in the pores of the wood block took place as the solution was stirred. There is involved a mechanical blocking in all three cases. Results of experiments typical of the three kinds of diffusion have been collected to form table 4. The solute used was urea, for which $D_w = 1.3 \times 10^{-5}$ at 25°C.

There have been summarized in table 5 the data for diffusion studies made on wood sections cut in the transverse direction. In the table heartwood is represented by the symbol Hw and sapwood is designated by Sw. Numbers in parenthesis after the kind of wood refer to the positions indicated by the chart, figure 2, which gives the location of the sample in the tree. The sample labeled 3a was taken next to the center but not concentric with it. Each figure in the table represents the average value of from six to twelve diffusion coefficients obtained from experiments on two to six samples of wood.

TABLE 2

Diffusion data for lactose into heartwood of white fir

Length of block = 3.14 cm.; R_w = 14.00; R_0 = 31.50

HOURS	R_t	$R_0 - R_t$	V	T	$D_s \times 10^6$
22.8	29.00	2.50	0.143	0.0205	0.248
46.8	28.10	3.40	0.194	0.0414	0.244
70.8	27.48	4.02	0.228	0.0615	0.240
94.8	27.00	4.50	0.257	0.0828	0.240
119.8	26.55	4.95	0.282	0.1062	0.244

TABLE 3

Effect of length of block on diffusion coefficient of glycerol into white fir heartwood (2)

BLOCK LENGTH	$D_s \times 10^5$
cm.	
1.35	0.46
1.38	0.45
1.41	0.46
2.09	0.44
3.14	0.44

It may be concluded from these data that a reproducible hindered or nearly free diffusion, of the type required for estimation of the mechanical blocking effect, results when observations are made on the *heartwoods* of pine, cedar, hemlock, and fir. It is also indicated that the structure of the sapwood in these species is too coarse to give consistent and reproducible diffusion constants.

The above data have been obtained with wood samples cut in the transverse direction. Diffusion into radial sections was also investigated and much lower diffusion constants resulted. Space does not permit the presentation and discussion of these data at the present time. Purely tangential sections of required length could not be cut from the trees

TABLE 4

Effect of pore size in determination of type of diffusion

Figures given are diffusion constants for urea, D_s

TIME INTERVAL	WHITE FIR HEARTWOOD (3) HINDERED DIFFUSION	WHITE FIR HEARTWOOD (2) APPROACHES FREE DIFFUSION	WHITE FIR SAPWOOD (1) STIRRED DIFFUSION (SLOW STIRRING)	WHITE FIR SAPWOOD (1) STIRRED DIFFUSION (RAPID STIRRING)
1	$0\ 34 \times 10^{-5}$	$0\ 64 \times 10^{-5}$	1.38×10^{-5}	1.66×10^{-5}
2	$0\ 36 \times 10^{-5}$	$0\ 66 \times 10^{-5}$	$1\ 34 \times 10^{-5}$	1.61×10^{-5}
3	0.34×10^{-5}	0.65×10^{-5}	1.31×10^{-5}	1.55×10^{-5}
4	0.35×10^{-5}	0.63×10^{-5}	1.19×10^{-5}	1.38×10^{-5}

TABLE 5

Diffusion data for wood samples cut in transverse section

WOOD	SOLUTE	SAMPLES	$D_s \times 10^5$	TYPE OF DIFFUSION
Cedar Sw (1)	Lactose	6	0.85–2.4	Stirred
Cedar Sw (1)	Glycerol	3	0.76–1.2	Stirred
Cedar Hw (2)	Glycerol	5	0.43	App. free
Cedar Hw (2)	Lactose	3	0.20	App. free
Cedar Hw (3a)	Lactose	3	0.13	Hindered
Cedar Hw (3)	Glycerol	2	0 25	Hindered
Cedar Hw (3)	Lactose	6	0.12	Hindered
Cedar Hw (3)	Urea	3	0 38	Hindered
Western hemlock Sw	Glycerol	2	0 26–0 93	Stirred
Western hemlock Hw	Lactose	2	0.18	App. free
Western hemlock Hw	Glycerol	3	0.43	App. free
White fir Sw (1)	Urea	3	0.86–1.55	Stirred
White fir Sw (1)	Lactose	3	0.52–1.51	Stirred
White fir Sw (1)	Glycerol	6	0.40–0.63	Stirred
White fir Hw (2)	Urea	3	0.67	App. free
White fir Hw (2)	Glycerol	6	0.44	App. free
White fir Hw (2)	Lactose	4	0.22	App. free
White fir Hw (3)	Glycerol	3	0 30	Hindered
White fir Hw (3)	Urea	3	0 36	Hindered

from which the sample blocks were taken. Several experiments with semi-tangential sections also gave much lower diffusion constants.

IV. DISCUSSION OF RESULTS

In the experiments in which a hindered or nearly free diffusion took place we assume D_s to be smaller than D_w for two reasons. The first and more important reason is the effect of the mechanical blocking, the second is the additional resistance to motion due to the proximity of the pit membrane pore walls to the diffusing solute molecule. Values of the fractional open area A have been calculated by the use of equation 2. In these calculations α is assumed to be zero and the pit membrane pore radii, based on Stamm's values, are for Western red cedar, 8 mμ, for Western hemlock, 12 mμ, and for white fir, 15 mμ. The values of A have been collected to form table 6. These values are shown by the points on figure 1.

TABLE 6

Fractional open area of transverse heartwood sections

SPECIES	SOLUTE	D_s	r/R	S	A
Western cedar (3)	Glycerol	0.25	0.05	0.70	0.32
Western cedar (3)	Lactose	0.12	0.10		0.32
Western cedar (3)	Urea	0.38	0.04		0.32
Western cedar (3a)	Lactose	0.13	0.10	0.70	0.36
Western cedar (2)	Glycerol	0.43	0.03	0.72	0.56
Western cedar (2)	Lactose	0.20	0.10		0.54
Western hemlock (Hw)	Glycerol	0.43	0.05	0.71	0.55
Western hemlock (Hw)	Lactose	0.18	0.08		0.48
White fir (3)	Glycerol	0.30	0.03	0.77	0.36
White fir (3)	Urea	0.36	0.02		0.30
White fir (2)	Glycerol	0.44	0.03	0.77	0.54
White fir (2)	Lactose	0.22	0.05		0.54
White fir (2)	Urea	0.67	0.02		0.54

The values of A fall into two regions, one at about 0.35 and the other at about 0.55, depending upon the distance from the center of the tree at which the sample was taken. Samples of heartwood taken at some distance from the center (region 2) give blocking coefficients which are but slightly below those required by the Dumanski equation. The differences between observed values and values obtained by calculation with the

Dumanski equation are probably due, in large measure, to the anisotropic character of the capillary spaces in the wood, and to aspirated tori. These samples are representative of the major area of the heartwood.

Samples of heartwood taken from the center (region 3) have *A* values lying much below the expectation based upon the use of the Dumanski equation, and even below that required by the Buckingham relation. These low values are not surprising when it is realized that the percentage of aspirated tori is high at the center of the tree. Furthermore, the actual effective value of the radii of the pores of the pit membranes is probably smaller than the value actually used in the calculations. A reduction of pit membrane pore radius for red cedar from 8 mμ to 4 mμ would cause an increase in blocking of 0.06 unit. Further, it must be recognized that the blocking factor changes more from the center to the periphery of the tree than would be expected from density measurements alone.

It is worthy of note that the data of table 6 are not inconsistent with rough estimates of the relative amounts of open and closed area of a wood section as determined by running a planimeter over photomicrographs of transverse wood sections. These estimates, made on photomicrographs which have been reproduced in articles by Ritter (12), indicate a fractional open area varying from 0.35 to 0.40.

The data obtained, therefore, may be considered to indicate the essential correctness of the theoretical deductions of Dumanski for the calculation of the mechanical blocking factor in a diffusion experiment involving a porous solid. We are not prepared to say as to whether or not the deviation between experiment and theory can be completely accounted for on the basis of the considerations presented above, because the apparent diffusion constants may be affected by the particle size and other factors not yet taken into account. The matter is deserving of further experimental work and theoretical analysis.

Finally, the data of this article are not without interest in connection with recent studies of Northrup and Anson (11) and of McBain (9, 10), in which the diffusion process has been caused to occur across thin porous membranes of alundum or glass powders, the idea being that the process would be greatly accelerated owing to the maintenance of a high concentration gradient, and at the same time, troublesome convection currents would be avoided. As Northrup and Anson point out, the pores must be small enough to prevent convection currents in the liquid held in them and large enough to allow free diffusion of the particles or molecules of the solute. It is evident from our table 4 that there is, between the two extremes, such a favorable capillary pore size in some wood sections for the diffusion of solute molecules of radius comparable to that of urea. It is only reasonable to suppose that there can be found other membranes having pore sizes to permit free diffusion of any given solute molecule and at the same time prevent convection currents.

In the method of Northrup and Anson a membrane is standardized against some solution, the diffusion constant of which is known, much after the fashion of the determination of the constant of a conductance cell. When the membrane constant for the diffusion apparatus with a particular diaphragm has been determined, it is used to obtain the diffusion coefficient for unknown substances. In this way any effects due to what we have termed mechanical blocking are eliminated.

Among other things this determination of membrane constant assumes invariable effective area of the pores. It would seem, therefore, that there still remains some uncertainty as to what effect, if any, there will be when the radius of the diffusing molecule is varied over such wide limits as has been the case in the investigations which have been carried out in this manner. At the present time we are inclined to agree with Kraemer (5), who writes, "This technic, however, combines the theoretical complications of osmotic pressure and free diffusion so that results obtained in this way for *D*, if presumed to be quantitative, can only be accepted as provisional until independent confirmation is obtained."

SUMMARY

1. Diffusion experiments in which the process is allowed to take place across the interface formed by a stirred liquid in contact with a gel have been extended to porous solids. The coefficients of diffusion at 25°C. of urea, lactose, and glycerol from aqueous solution into transverse sections of samples of white fir, Western hemlock, and Western red cedar wood have been determined.

2. From the data obtained it has been possible to distinguish three kinds of diffusion. They have been described as hindered diffusion, free diffusion, and stirred diffusion. Attention has been called to results of experiments which are typical of each. These data are of interest in connection with recent methods which have been proposed for the determination of the diffusion coefficient of a solute from its rate of passage through a thin porous membrane.

3. Fractional open areas for heartwood sections have been calculated by using a modified theory, when it could be shown that the diffusion constant was not influenced by the rate of stirring. Comparisons of the experimentally observed mechanical blocking factors with those calculated by the theoretical and empirical equations already existent in the literature have been made.

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A STUDY OF CERTAIN FACTORS INFLUENCING THE MOVEMENT OF LIQUIDS IN WOOD[1]

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Early workers in the fields of plant anatomy and physiology did not believe there were any direct openings between the cells of wood. To explain the movement of viscous organic substances, preserving oils for example, Tiemann (21) advanced the hypothesis that the wood was made permeable by checks which developed in the cell wall during seasoning. Weiss (22) modified this hypothesis to explain why a greater penetration of preserving oils was obtained in the dense summerwood of longleaf pine. Information was later submitted by Bailey (1, 2) which led him to conclude that the intercellular movement of preserving fluids was through small openings in the pit membranes. Scarth (14), after an examination of coniferous wood impregnated with mercury, also concluded that the effective intercellular communication was localized in the bordered pits.

Assuming that the pit membrane pores were the means of intertracheid flow, Stamm (15) has used physical methods to obtain the dimensions of the pit perforations. The range in average diameters (of true circles having the same effect as the openings of unknown shape) of the pit perforations in two species was found to be 11 mμ to 23 mμ. The range in maximum diameters for five woods was found to be 68 mμ to 184 mμ. Stamm (16) also has recently made determinations of the ratio of the effective capillary length to the effective capillary cross section of the pores in the pit membranes.

The influence of certain of the gross structural features of wood upon the movement of liquids has been investigated by a number of workers. Griffin (5, 6) and MacLean (13) have obtained evidence that the position of the tori of the bordered pits influences the permeability of wood. Teesdale (18) and Teesdale and MacLean (19) found that the distribution of resin canals and the freedom of vessels from obstructions are other structural features which influence the impregnation of wood. These studies clearly showed, however, that wood of similar gross structure may react quite differently to impregnation.

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Investigations have been made of the effect of pressure upon the rate of flow of liquids through wood. Johnston and Maass (9), referring to the influence of pressure, state: "The rate of flow in greenwood and sapwood tends to increase in proportion to the pressure when the system is in a stable state, but in seasoned wood, flow increases more rapidly especially at the higher pressures, when even sapwood departs from a linear relationship." On the other hand Sutherland, Johnston, and Maass (17) have reported that the rate of flow of water through seasoned and unseasoned white spruce and the unseasoned heartwood of black spruce was approximately proportional to the pressure. For the unseasoned heartwood of Norway pine, cedar, tamarack, balsam fir, and white pine a disproportionate increase in rate of flow was obtained for increased pressures.

Teesdale and MacLean (20), in an early work, found no apparent relationship between viscosity (expressed in Engler numbers) and the ease of movement of mixtures of coal-tar creosote and coal tar in the heartwood of longleaf pine. Bateman (3) recalculated their data and concluded that when the viscosity was expressed in centipoises a definite relationship between the viscosities of the preserving oils and their penetrations into wood did exist. MacLean (10, 11, 12, 13) in later work emphasized the importance of the relationship between absolute viscosity and the penetration into wood of aqueous solutions of zinc chloride, mixtures of coal-tar creosote and petroleum, and coal-tar creosotes. Howald (7, 8) found, however, that the penetrations of certain petroleums and mixtures of coal-tar creosote and petroleum could not be predicted from their viscosities. Likewise Johnston and Maass (9) have observed deviations from purely viscosity considerations for aqueous solutions of neutral sulfites when the rates of flow of these solutions were compared with water, and Sutherland, Johnston, and Maass (17) have obtained similar results for aqueous solutions of glucose.

EXPERIMENTAL

The problem

We have studied certain of the relationships governing the pressure movement of liquids in wood. These were: (1) the influence of moisture content of wood below the fiber-saturation point upon the relative effectiveness of the intercellular openings, (2) the influence of pressure upon the rate of flow of water through wood, and (3) the movement of organic liquids and salt solutions through wood.

Apparatus and methods

The effect of moisture content upon the pressure necessary to overcome the surface tension of benzene in the maximum effective intercellular openings in wood was determined with an apparatus similar to that described by Stamm (15).

The rate of flow of different organic liquids through wood and the rate of flow of water at different pressures was determined by the use of an apparatus made of brass. A similar apparatus made from glass was employed for the study of the movement of salt solutions. The two sets of apparatus were composed of the essential parts shown in figure 1.

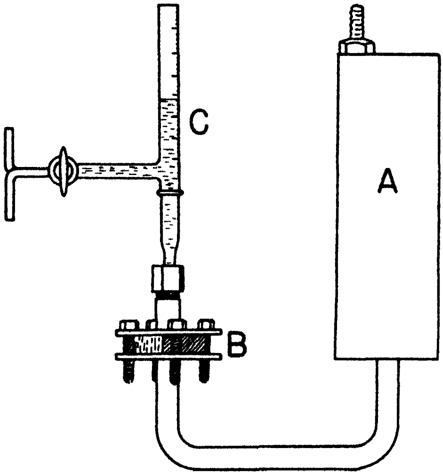

FIG. 1. THE ESSENTIAL FEATURES OF THE APPARATUS USED IN DETERMINING THE RATE OF FLOW OF LIQUIDS THROUGH WOOD

Air pressure was applied to the liquid in the supply tank, A, which forced it through the wood section held in place at B (the area of the section exposed to the path of flow of the liquid was 0.35 sq. cm. for the brass apparatus and 1.93 sq. cm. for the glass apparatus), and into the buret, C. An air pressure gauge sensitive to 0.05 kg. per square centimeter and a mercury manometer were employed for measuring the applied air pressure.

The temperature was not controlled. However, each time a reading was taken the room temperature was recorded. These results showed that the normal fluctuations in temperature of the room did not appear to influence materially the relationships obtained.

The viscosity of the kerosene was determined with an Ostwald viscometer. The viscosities of the other organic liquids were determined by interpolation from values obtained from the International Critical Tables.

The moisture content given in all cases is expressed in terms of percentage of the oven-dry weight, which was determined by drying to constant weight at 105°C. at atmospheric pressure in an electric oven.

Materials

Seven kinds of wood were used: namely, balsam (*Abies balsamea* (Linneaus) Miller), Norway pine (*Pinus resinosa* Solander), white spruce (*Picea glauca* (Moench) Voss), Northern white cedar (*Thuja occidentalis* Linnaeus), Western red cedar (*Thuja plicata* D. Don), and Eastern hemlock (*Tsuga canadensis* (Linnaeus) Carrière).

All Norway pine, balsam fir, and white spruce sections were sawed from freshly felled logs. The Northern white cedar, Western red cedar, and Eastern hemlock sections were sawed from air-dry material, the past history of which was unknown. In all cases transverse sections more than one tracheid length in thickness, sawed from clear pieces of wood cut parallel with the grain, were employed. The numbers by which the wood sections in each group are designated indicate their relative positions in the original piece of wood.

The following liquids and chemicals were used: water (freshly distilled), hexane (Eastman, Practical Grade), nitrobenzene (Eastman, C.P.), bromobenzene (Eastman, C.P.), kerosene ("composed of predominantly straight chain hydrocarbons" furnished by The Atlantic Refining Company), benzene (C.P., thiophene-free), and inorganic salts (C.P.).

THE EXPERIMENTAL FINDINGS

The influence of moisture content upon the permeability of wood

In all of Stamm's work (15), dealing with the determination of the maximum effective diameters of the pores in the pit membranes of coniferous wood, water was the liquid displaced from the pit membrane capillaries. The pore sizes consequently were those existing at the fiber-saturation point. It seemed of interest therefore to investigate the influence of varying amounts of water present in the cell wall upon the maximum effective diameters of the openings between the cells. This was done by determining the pressure necessary to overcome the surface tension of benzene in sections of balsam fir heartwood (1.40 cm. in thickness) which were at different moisture contents. These sections were sawed from a freshly felled log and slowly dried to approximately 6 per cent in moisture content. They then were transferred to three chambers in which different relative humidities were maintained, and were permitted to take up moisture until they had reached approximate equilibrium. Taken from the different humidity conditions the sections were immediately submerged in benzene, and determinations made of the gas pressure necessary to overcome the surface tension of benzene in the maximum effective intercellular openings. The values obtained in this manner may be used for comparative purposes as being inversely proportional to the maximum effective openings through the wood section. The data are shown graphically in figure 2. The result for each moisture content is an average for five wood sections.

Another method of ascertaining the influence of moisture content upon the effective size of the openings between the cells of wood also was employed. This consisted of determining the rate of flow of an organic liquid through wood sections which had been previously brought to equilibrium with different relative humidities. This method gives a basis of comparison for the change in effectiveness of the average diameters of the openings between the cells of wood; the more rapid the rate of flow the greater the effectiveness of the average diameters.

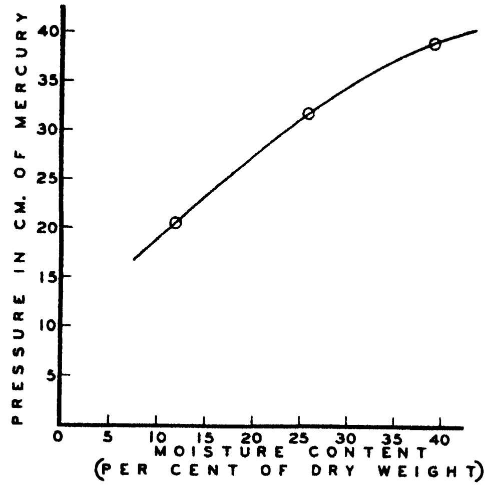

FIG. 2. THE EFFECT OF MOISTURE CONTENT UPON THE PRESSURE REQUIRED TO OVERCOME THE SURFACE TENSION OF BENZENE IN THE MAXIMUM EFFECTIVE INTERCELLULAR OPENINGS OF BALSAM FIR HEARTWOOD

Sections of Norway pine (1.3 cm. in thickness) were sawed from freshly felled logs and slowly dried to approximately 6 per cent moisture content. After drying the sections were permitted to take up moisture to equilibrium with different relative humidities. These sections then were taken from the different relative humidities, submerged in the organic liquid, and determinations made immediately of the rate of flow of the organic liquid through them. The average rate of flow in cubic centimeters per minute for the first 10 cc. forced through the section was taken as the measure of permeability. Care was taken not to allow any appreciable exposure of the sections to the air; while the sections were in the apparatus they were surrounded by a bath of the organic liquid which prevented any appreciable loss of moisture.

The results obtained for the rate of flow of benzene, a non-polar organic liquid, through Norway pine sapwood are shown graphically in figure 3. The rate of flow for each moisture content is an average for two wood sections. A pressure of 26.0 cm. of mercury was used for all of these determinations.

The data for the rate of flow of nitrobenzene, a polar organic liquid, through Norway pine sapwood at different moisture contents are given in table 1. A pressure of 119.8 cm. of mercury was used for all of these determinations.

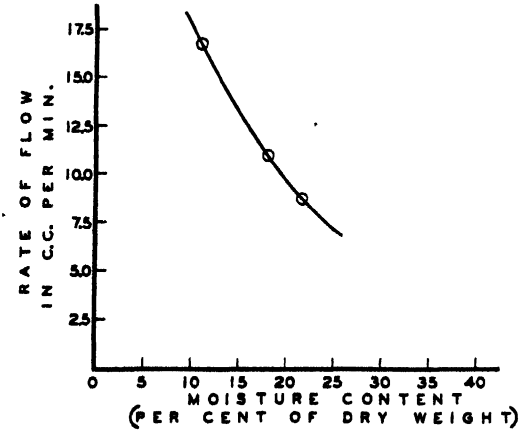

FIG. 3. THE EFFECT OF MOISTURE CONTENT UPON THE RATE OF FLOW OF BENZENE THROUGH NORWAY PINE SAPWOOD

Pressure, 26.0 cm. of mercury

Assuming that the intercellular openings in wood are through the membranes of the pits, the data in figures 2 and 3 and table 1 show that the maximum and average effective diameters of the pores in the pit membranes became smaller with increasing moisture content of the wood below the fiber-saturation point. The results do not, however, offer an exact measure of the change in effectiveness of these openings with moisture content. Factors such as slight changes in moisture content during the handling of the sections and the possibility of flow through the resin canals of Norway pine would tend to modify the relationship between the effective diameters of the openings in the pit membranes and moisture content. The results can therefore only be interpreted as illustrating the trend of the influence of the moisture content of wood below the fiber-saturation point upon the effective diameters of the openings in the pit membranes.

Influence of pressure upon the rate of flow of water through wood

Sections of balsam fir (1.10 cm. in thickness), Norway pine sapwood (1.24 cm. in thickness), white spruce sapwood (1.33 cm. in thickness), Northern white cedar (1.24 cm. in thickness), Western red cedar (1.18 cm. in thickness), and Eastern hemlock (1.35 cm. in thickness) were used in these experiments. The balsam fir, Norway pine, and white spruce sections were obtained from freshly felled logs. Paired sections of each of the three woods were divided into two groups. Sections of one group were given a seasoning treatment, while those of the other group were immediately placed in distilled water. The Norway pine and white spruce sections designated as seasoned, were slowly dried to approximately 4 per cent moisture content. The balsam fir sections designated as seasoned were first dried to approximately 4 per cent moisture content and then were dried to a constant weight at 105°C. (a 6-hour drying period was used). The Northern white cedar, Western red cedar, and Eastern hemlock sections were obtained from air-dried material which had a moisture content of approximately 8 per cent at the time of preparation. These sections, together with the seasoned sections of balsam fir, Norway pine and white spruce, were placed in distilled water.

TABLE 1

Effect of moisture content upon the rate of flow of nitrobenzene through Norway pine sapwood

Pressure 119.8 cm. of mercury

NUMBER OF THE SECTION	MOISTURE CONTENT OF THE SECTION*	RATE OF FLOW
	per cent	*cc. per minute*
9	Av. = 6 56	6 70
24		21 05
34		10 43
		Av. = 12 73
2	Av. = 15 65	2 54
22		5 31
33		4 69
		Av. = 4 18

* The moisture content given is an average obtained for three sections similarly treated.

Both the seasoned and unseasoned sections were allowed to soak for at least two weeks before testing their permeability. The soaking was carried out in a desiccator, and an intermittent vacuum was applied to facilitate the complete removal of air from the cells.

After the soaking period the sections were placed in the apparatus and water forced through them until an approximately constant rate of flow was obtained. In attaining the constant rate of flow a decreasing rate of flow with time from the initial rate was observed in all cases except in several runs with white spruce sapwood. In these runs it was observed that the decreasing rate of flow was preceded by an increase from the initial rate. After a constant rate of flow had been obtained, higher pressures were applied and the new rate of flow determined for each of the pressures. Values for the rate of flow then were obtained by decreasing the pressure and observing the rate of flow at lower pressures. The values obtained in this manner were in close agreement for the same pressure whether the rate of flow was determined by going from a lower to higher pressure or *vice versa*, providing that sufficient time was allowed for the sections to return to a constant rate with the lower pressures. In the case of white spruce and Norway pine it was observed that the return to the constant rate of flow was very rapid. In the case of balsam fir and the other woods which gave a pronounced disproportionate rate of flow with increased pressures, it was observed that longer periods of time were required to return to a constant rate of flow with the lower pressures. The results obtained for the rate of flow of water through both seasoned and unseasoned woods are given in table 2. The value given in each case is an average of the results for three sections of each wood both seasoned and unseasoned.

The data given in table 2 and figure 4 show that the influence of pressure on the rate of flow is characteristic of the kind of wood. Seasoning of the wood previous to use did not significantly alter the relationship between pressure and the rate of flow for white spruce, Norway pine, and balsam fir. This is particularly illustrated by the results for balsam fir, because the unseasoned sections of this wood were not dried after they were sawed from a freshly felled log, while the seasoned sections were oven-dried. Table 3 gives the results for both the seasoned and unseasoned individual sections of balsam fir heartwood.

Likewise seasoning did not appear to cause any pronounced permanent changes in the permeability of the woods to water. This would seem to indicate that when the sections were seasoned in the manner previously described, either seasoning did not increase pit aspiration in the manner observed by Griffin (5) or more importance has been attributed to this condition than it deserves. In fact, in the cases of balsam fir and white spruce the rate of flow was more rapid at any pressure for the seasoned than for the unseasoned wood. For Norway pine the situation was reversed; the unseasoned wood was the more permeable. However, the

TABLE 2

Influence of pressure upon the rate of flow of water through seasoned and unseasoned coniferous woods

KIND OF WOOD	TREATMENT	PRESSURE	RATE OF FLOW	RATE OF FLOW
		kg. per sq. cm.	*cc. per minute*	*per cent*
Balsam fir heartwood	Seasoned (oven-dried)	1.8	0 092	2.56
		3.5	0 534	14.85
		5.3	1.553	43.19
		7.0	3.596	100.00
Balsam fir heartwood	Unseasoned	1.8	0.062	2.34
		3.5	0.429	16.19
		5.3	1.186	44.75
		7.0	2.650	100.00
Norway pine sapwood	Seasoned	1.8	2.35	16.78
		3.5	5.83	41.64
		5.3	9.66	69.00
		7 0	14.00	100.00
Norway pine sapwood	Unseasoned	1.8	3.01	20.62
		3.5	6.60	45.21
		5.3	10.61	72.67
		7.0	14.60	100.00
White spruce sapwood	Seasoned	1 8	0.171	25.15
		3.5	0.345	50.73
		5 3	0.507	74.56
		7.0	0.680	100.00
White spruce sapwood	Unseasoned	1.8	0.141	25.59
		3.5	0 289	52.45
		5.3	0 425	77.13
		7.0	0.551	100.00
Northern white cedar heartwood	Seasoned	1 8	0.082	4.83
		3.5	0.392	23.09
		5.3	0.971	57.18
		7.0	1.698	100.00
Western red cedar heartwood	Seasoned	1.8	0.237	3 66
		3.5	1.580	24.39
		5.3	3.722	57.46
		7.0	6.477	100.00
Eastern hemlock heartwood	Seasoned	1 8	0 157	5.27
		3.5	0.725	24.34
		5.3	1.657	55.64
		7.0	2 978	100.00

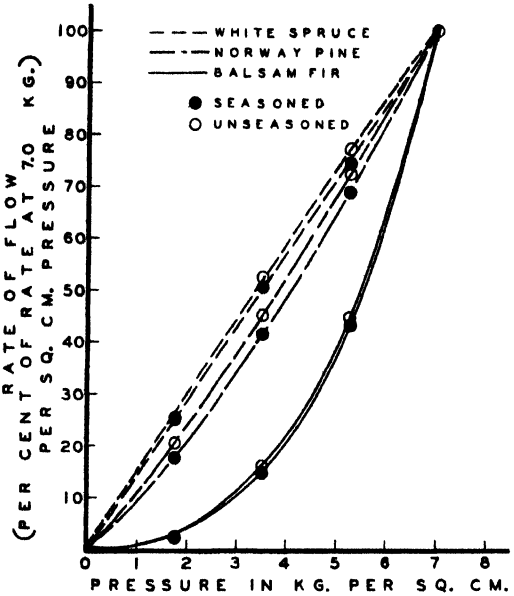

FIG. 4. THE EFFECT OF PRESSURE UPON THE RATE OF FLOW OF WATER THROUGH SEASONED AND UNSEASONED BALSAM FIR HEARTWOOD, NORWAY PINE SAPWOOD, AND WHITE SPRUCE SAPWOOD

TABLE 3

Variability of the influence of pressure upon the rate of flow of water through seasoned and unseasoned balsam fir heartwood

TREATMENT	PRESSURE	RATE OF FLOW					
		Section No 19		Section No 21		Section No. 26	
	kg. per sq. cm	*cc. per minute*	*per cent*	*cc. per minute*	*per cent*	*cc per minute*	*per cent*
Unseasoned........	1.8	0.084	1 90	0.058	2.61	0.044	3.26
	3.5	0.722	16.30	0 333	15.00	0 231	17 11
	5.3	2.009	45 36	0 969	43.65	0.580	42.96
	7 0	4.429	100.00	2.220	100.00	1.300	100 00
		Section No. 16		Section No. 20		Section No. 22	
		cc. per minute	*per cent*	*cc. per minute*	*per cent*	*cc. per minute*	*per cent*
Seasoned (oven-dried)............	1.8	0.132	2.52	0.081	2.79	0.064	2.41
	3.5	0.771	14.74	0.441	15.20	0.391	14.72
	5.3	2.213	42.30	1.301	44.85	1.145	43.11
	7.0	5.232	100.00	2.901	100.00	2.656	100.00

differences in observed permeability were within the limits of variation of individual samples treated in the same manner, and for this reason caution is necessary in the interpretation of the results.

The results obtained for the relationship between pressure and the rate of flow of water through Norway pine, white spruce, balsam fir, and Northern white cedar are in general agreement with those reported by Sutherland, Johnston, and Maass (17) for heartwood of the same four woods. Sutherland, Johnston, and Maass concluded that the different relationships between pressure and rate of flow obtained for different woods perhaps could be explained on the basis of a varying thickness of the effective pit membranes. They reasoned that pressure would cause a stretching of the thin pit membranes, resulting in an increase in size of the pit membrane pores, and consequently the relative importance of this effect of pressure would vary for pit membranes of different thickness.

It also seems possible that the effect of pressure on the rate of flow of liquids through coniferous wood may be modified somewhat by the presence of structures such as resin canals. Of the six woods used in this study Norway pine and white spruce possess resin canals, while the other woods do not. If we assume, as has been done in this study, that the flow of liquids between tracheids is through the pores in the pit membranes, it follows that for woods which do not possess resin canals the flow was entirely of this type. For white spruce and Norway pine the resin canals may have contributed to the flow. If this is the case, then it is certainly conceivable that a different relationship between pressure and rate of flow exists when a portion of the liquid is moving through a comparatively large opening such as a resin canal, than when the movement is confined to the small openings in the thin pit membranes.

The movement of organic liquids and aqueous salt solutions through wood

Sections of balsam fir heartwood (1.00 cm. in thickness) and Norway pine sapwood (1.33 cm. in thickness) sawed from freshly felled logs were used in these determinations.

The sections used with the organic liquids were gradually dried to equilibrium under controlled humidity. Moisture determinations made after the sections had attained equilibrium showed that two samples of Norway pine sapwood had moisture contents of 24.63 per cent and 24.71 per cent, and two samples of balsam fir heartwood had moisture contents of 21.08 per cent and 21.01 per cent.

The sections were taken from the humidity chambers and transferred to the apparatus in weighing bottles. Thus the sections were not exposed to the air for any appreciable length of time. The term "initial rate of flow" is used to designate the rate of flow after 1 cc. of the liquid had been forced through the section.

TABLE 4

Rate of flow of several organic liquids and water through balsam fir heartwood

Pressure 1.8 kg. per square centimeter

TIME		HEXANE		BENZENE		WATER		BROMOBENZENE		KEROSENE		NITROBENZENE	
		Section No 2	Section No 11	Section No. 4	Section No. 12	Section No. 6	Section No 7	Section No 8	Section No. 14	Section No. 5	Section No. 9	Section No. 1	Section No. 10
Rate of flow in cc. per minute													
hours	*minutes*												
0	00	2.500	2.308	1.600	1.429	1.091	0.800	1.200	1.463	0.984	0.923	0.282	0.209
0	30	2.222	2.069	1.429	1.333	0.582	0.385	0.800	1.071	0.698	0.606	0.0977	0.0904
1	30	2.143	1.936	1.367	1.250	0.375	0.235	0.594	0.800	0.606	0.526	0.0640	0.0549
2	30	2.105		1.333	1.200	▶	0.167		0.667	0.556	0.456	0.0526	0.0400
3	30		1.875			0.239	0.142				0.415	0.0456	0.0310
4	30							0.432				0.0319	0.0243
5	30						0.120	0.417					0.0210
Rate of flow in percentage of the initial rate													
0	00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
0	30	88.88	89.64	89.31	93.28	53.34	48.12	66.67	73.20	70.94	65.66	34.64	43.25
1	30	85.72	83.88	85.44	87.47	34.37	29.38	49.50	54.68	61.59	56.99	22.69	26.27
2	30	84.20		83.31	83.97		20.88		45.59	56.50	49.40	18.65	19.14
3	30		81.24			21.91	17.75				44.96	16.17	14.83
4	30							36.00				11.31	11.63
5	30						15.00	34.75					10.05
Viscosity at 25°C. in centipoises		0.33		0.60		0.89		1.07		1.23		1.85	

The results for the rate of flow through balsam fir heartwood are given in table 4. A pressure of 1.8 kg. per square centimeter was used for all of these determinations.

The values given in table 4 for the rate of flow in cubic centimeters per minute of nitrobenzene (section No. 10), kerosene (section No. 9), and water (section No. 7) are shown graphically in figure 5. The values given in table 4 for the rate of flow in percentage of the initial rate for sections Nos. 7, 8, 9, 10, 11, and 12 are shown graphically in figure 6.

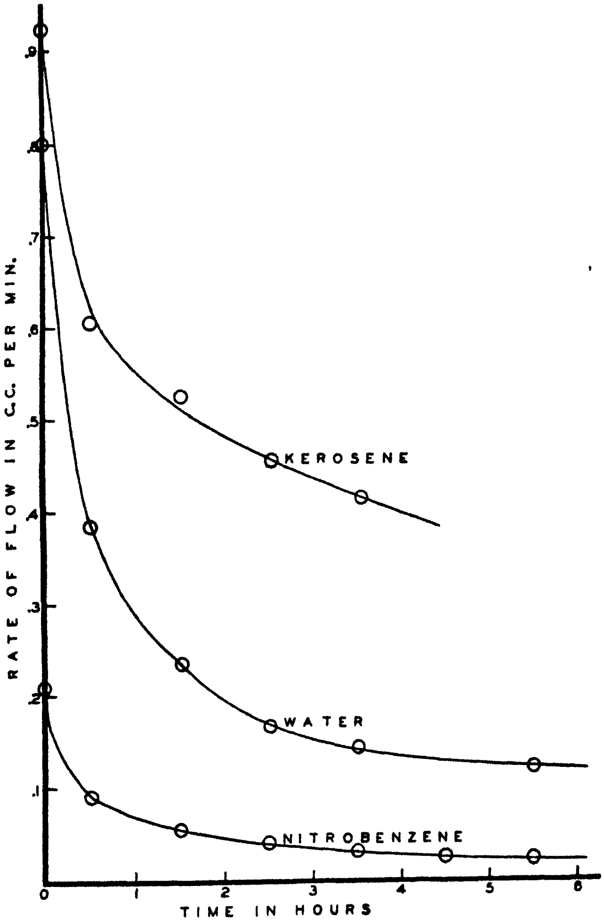

FIG. 5. RATE OF FLOW OF KEROSENE, WATER, AND NITROBENZENE THROUGH BALSAM FIR HEARTWOOD

Pressure, 1.8 kg. per square centimeter

Table 5 gives the data for the rate of flow of benzene, kerosene, and nitrobenzene through Norway pine sapwood. A pressure of 23.0 cm. of mercury was used for all of these determinations.

The balsam fir heartwood sections used with the aqueous salt solutions were submerged in distilled water immediately after preparation and allowed to soak for at least two weeks under the influence of an intermittent vacuum. The sections then were placed in the apparatus and water forced through them, under a pressure of 76.5 cm. of mercury, until an equilibrium rate of flow was obtained. The water then was replaced with the desired salt solution. The initial rate of flow and the change in rate of flow with time were determined for the salt solution. The initial rate of flow in this case was the value observed after approximately 0.5 cc. of the solution had been forced through the section. The salt solutions used were 0.1 normal solutions of zinc chloride, potassium chloride, mercuric chloride, and aluminum chloride, and a 0.01 normal solution of thorium chloride. The results for the different salt solutions are shown graphically in figure 7. The rate of flow is expressed as a percentage of the equilibrium rate of flow for water.

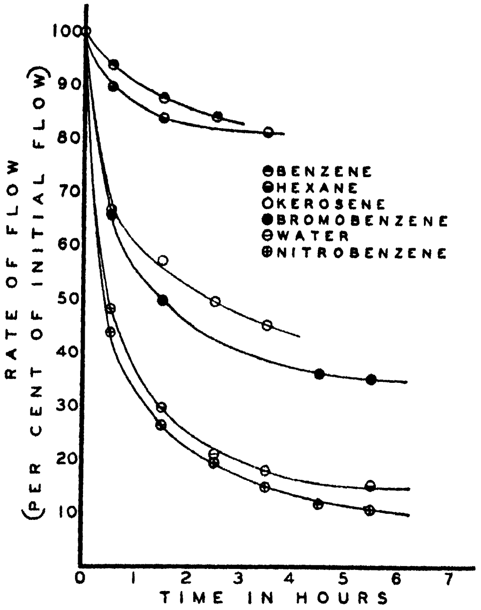

FIG. 6. CHANGES IN THE RATE OF FLOW WITH TIME OF WATER AND SEVERAL ORGANIC LIQUIDS THROUGH BALSAM FIR HEARTWOOD

Pressure, 1.8 kg. per square centimeter

The data given in tables 4 and 5 and figures 5, 6, and 7 show that the rate of flow of liquids of widely different properties through wood cannot be predicted necessarily from their viscosities. The data in table 4 show that kerosene having a viscosity of 1.23 centipoises gave an initial rate of flow approximately four times that for nitrobenzene and a rate of flow at the end of 3.5 hours about thirteen times that for nitrobenzene. Water with a viscosity of 0.89 centipoise, had an initial rate of flow slightly less than that for kerosene and a rate of flow at the end of 3.5 hours approximately one-third the rate for kerosene and four times the rate for nitrobenzene. From the standpoint of a direct viscosity relationship, the rate of flow for water should be about twice the rate for nitrobenzene, but the value actually obtained was about four times the rate. Also on the basis of purely viscosity considerations the rate of flow of benzene should have been about three times the rate for nitrobenzene, yet the initial rate for benzene was about six times and at the end of 2.5 hours was about twenty-seven times the value for nitrobenzene.

TABLE 5

Rate of flow of several organic liquids through Norway pine sapwood

Pressure 23.0 cm. of mercury

TIME		BENZENE		KEROSENE		NITROBENZENE	
		Section No 37	Section No. 40	Section No. 38	Section No. 39	Section No. 28	Section No. 36
		Rate of flow in cc. per minute					
hours	*minutes*						
0	00	7 500	5 854	4 000	2 670	1 163	1 463
0	30	8 570	5 333	3 200	2 449	0 566	0 895
1	30	8 450	5 217	2 105	1 644	0 486	0 674
2	20	7 321	5 217	1 644	1 333	0 392	0.529
3	30			1.558	1 121	0 344	0 400
4	30			1 500		0 314	0 360
5	30					0 289	0.322
6	30						0.312
		Rate of flow in percentage of the initial rate					
0	00	100 00	100 00	100 00	100 00	100 00	100.00
0	30	114 57	91 10	80 00	91 72	48 67	61.18
1	30	112 67	89.12	52 62	61 57	41 79	46.07
2	80	97 61	89 12	41 10	49 92	33 71	36 16
3	30			38 95	41 98	29 58	27 34
4	30			37 50		27.00	24 61
5	30					24 85	22.01
6	30						21.33
Viscosity at 25.0°C. in centipoises		0 60		1 23		1 85	

The relationships obtained for Norway pine sapwood, table 5, are in general agreement with those obtained for balsam fir heartwood. However, the differences in rates of flow of the different liquids were not of the same magnitude as those for balsam fir heartwood.

The data given in figure 7 show that pronounced deviations from purely viscosity considerations exist for the flow of different salt solutions through balsam fir heartwood. The zinc chloride solution flowed through the wood sections more than three times as rapidly as water, while the rate of flow of the thorium chloride solution was only about one-sixth as rapid as water. These differences are more pronounced if the two salt solutions are compared. When considered in this manner, the rate of flow of the zinc chloride solution through balsam fir heartwood was approximately eight-

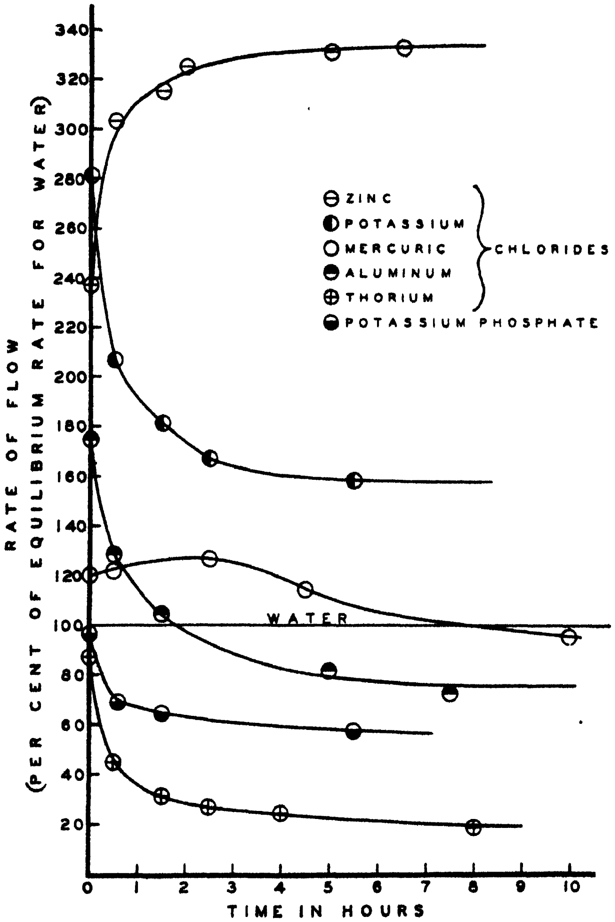

FIG. 7. CHANGES IN THE RATE OF FLOW WITH TIME OF SEVERAL SALT SOLUTIONS THROUGH BALSAM FIR HEARTWOOD

Pressure, 76.5 cm. of mercury

een times that of the thorium chloride solution, yet the viscosities of the different salt solutions, for the concentrations used, are not greatly different from that of water.

The results obtained for the flow of organic liquids and salt solutions through coniferous wood show that factors other than viscosity determine in a considerable measure the rates of flow through wood of liquids possessing widely different properties. Factors such as the influence of the liquids upon the effective diameters of intercellular openings must be considered. Shrinking, swelling, or a solution of materials from these openings would alter the rate of flow of liquids through wood. Bull (4) also has pointed out that with small capillaries (0.1 μ) electrical "back pressure" may play an important rôle in the flow of organic liquids such as nitrobenzene. In addition, polar liquids such as nitrobenzene should be expected to be strongly adsorbed and highly oriented on the surface of the pit membrane capillaries. It may well be that these adsorbed oriented molecules are an effective agent in reducing the area of the pores in the pit membranes; certainly they, as well as the tetravalent thorium ions, will materially affect the surface electrical properties of such capillary openings.

A comparison of the results obtained for the flow of organic liquids through Norway pine sapwood and balsam fir heartwood indicates that the relative importance of factors other than viscosity would vary with the kinds of wood. It seems that different woods may be expected to show different behavior. The presence and effectiveness of structures such as resin canals, variation in the size of the pores in the pit membranes, and the presence of extraneous materials such as resins in the effective openings of the pit membrane pores are perhaps only some of the factors which would tend to make one wood behave differently from another.

SUMMARY

1. A study was made of: (1) the relative effectiveness of the maximum and average pore diameters of the openings in the pit membranes for wood at different moisture contents, (2) the influence of pressure upon the rate of flow of water through wood, and (3) the movement of organic liquids and salt solutions through wood.

2. The maximum and average effective diameters of the pores in the pit membranes were found to vary with the moisture content of the wood: below the fiber-saturation point effective pore diameters decreased with increasing moisture content.

3. The influence of pressure upon the rate of flow of water through wood is a characteristic of the kind of wood.

4. The relationship between pressure and the rate of flow of water through wood perhaps is influenced by factors such as the thickness of the pit membrane and the presence and effectiveness of resin canals.

5. The relationship between pressure and the rate of flow of water through several woods was not changed significantly by drying of the wood previous to use.

6. Drying previous to use did not appear to cause pronounced permanent changes in the permeability of the woods to water.

7. The rate of flow of organic liquids and aqueous salt solutions could not be predicted necessarily from the viscosities of these liquids. The same was true for the rate of flow of organic liquids through Norway pine sapwood.

8. Evidence was obtained which indicates that the magnitude of the deviations from a viscosity relationship for the flow of organic liquids would be different for different kinds of wood.

9. The decrease in rate of flow with time through balsam fir heartwood for benzene, bromobenzene, and nitrobenzene increased with increasing polarity of the liquid.

10. It would seem that the movement of liquids of widely different properties in wood cannot be predicted necessarily from the viscosity alone. Other factors such as the influence of the liquid upon the effective capillary dimensions of the openings in wood and the possible effect of electrical "back pressure" on the flow of polar organic liquids must be considered. The relative importance of factors other than viscosity can perhaps be expected to vary with the kinds of wood and the properties of the liquids.

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THERMODYNAMICS OF THE SWELLING OF WOOD

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Although the swelling of a number of colloidal materials has been studied intensely, little attention has been given the thermodynamic aspects of swelling. This lack of attention is perhaps because the major part of sorption and swelling data are not subject to thermodynamic calculations. Katz (2) has pointed out that thermodynamics deals only with true equilibrium conditions and hence such effects as those of sorption and swelling hysteresis and changing surface of sorption during a single cycle must be eliminated in order that the results have theoretical significance.

Katz (2) has compared the differential heats of swelling in water obtained from thermal data with the changes in free energy of swelling calculated from moisture content–vapor pressure data for cotton, wood, and casein, using the equation

$$- \Delta F = \frac{RT}{M} \ln \frac{P}{P_0} \tag{1}$$

in which $-\Delta F$ is the change in free energy in gram-calories occurring when 1 g. of liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the relative vapor pressure $\frac{P}{P_0}$, R being the gas constant, T the absolute temperature, and M the molecular weight of the liquid. Since the differences between the differential heats of swelling and the changes in free energy of swelling were small, he concluded that they were within the range of experimental error and that consequently the entropy change was negligible.

Fricke and Lüke (1), however, have shown that this is by no means the case. They determined both the integral heat of swelling at different moisture content values and the moisture content–relative vapor pressure relationship at two different temperatures for agar-agar, casein, and keratin swelling in water. They were thus able to calculate the differential heat of swelling, using the integrated form of the Clausius-Clapeyron equation

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[1] Maintained at Madison, Wisconsin, by the Forest Service of the U. S. Department of Agriculture, in coöperation with the University of Wisconsin.

$$\Delta H = \frac{RT_1T_2}{M(T_2 - T_1)} \ln\left(\frac{P_2}{P_1} - \frac{P_{0_2}}{P_{0_1}}\right) \tag{2}$$

in which ΔH is the change in the heat of swelling in gram-calories occurring when 1 g. of the liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the vapor pressure P_2 at the temperature T_2 and the vapor pressure P_1 at the temperature T_1, P_{0_2} and P_{0_1} being the corresponding saturation vapor pressures and the other symbols having the same significance as in equation 1. In these calculations as well as in those for obtaining $-\Delta F$ the averages between desorption and adsorption moisture contents corresponding to each relative vapor pressure were used as an approximate means of eliminating the effects of hysteresis. The values for ΔH calculated in this way agreed very well with the values obtained from the thermal measurements, thus substantiating the validity of the theoretical equation. Values of $-\Delta F$ calculated from the vapor pressure data were in all cases less than the corresponding values of ΔH, showing that a definite entropy change ΔS accompanies swelling; thus

$$\Delta S = \frac{\Delta H - (-\Delta F)}{T} \tag{3}$$

Katz (3) has recently admitted the validity of Fricke and Lüke's findings, and suggests that the increase in entropy occurring during swelling is due to an orientation or compression of the water molecules, which become adsorbed on the surface of the swelling material, or to an association of these molecules.

In connection with a study of the seasoning of wood, the Forest Products Laboratory recently had occasion to collect moisture content–relative vapor pressure–temperature data on the drying of wood. As these data were obtained under conditions which practically eliminate hysteresis effects, it seemed worth while to subject them to thermodynamic analysis.

The equilibrium moisture content determinations were made in four specially designed drying chambers, each of which had a capacity of about 16 cu. ft. The chambers were equipped with electrically driven blowers which moved the air uniformly through the drying compartments at a rate of about 100 ft. per minute. The wet- and dry-bulb temperatures in each kiln were under the control of a thermostat of the vapor tension type. The drying conditions in the chambers were read frequently through glass windows.

The dry-bulb temperature oscillated on an average about ¼°F. above and below the desired value, while the wet-bulb temperature had a total positive and negative amplitude of about ½°F. The wet- and dry-bulb cycles would sometimes be out of phase 180°, with the result that the wet-bulb depression was sometimes ¾°F. greater or less than desired. The maximum amplitude of relative vapor pressure oscillations at the higher temperatures was from 1.5 to 3.0 per cent for different vapor pressures, and at the lower temperatures from 4.0 to 8.0 per cent.

From twenty-five to forty strips of green flat-sawed Sitka spruce were used in determining the equilibrium moisture content for a given temperature and relative vapor pressure. The strips were cut about 3 mm. thick and weighed from 100 to 125 g. each when in an oven-dry condition. The specimens were suspended from lead stoppers located in the roof of the chambers and were weighed *in situ* during the drying process to 0.05 g.

The hysteresis phenomenon encountered in desorption and adsorption measurements made on very small specimens under the most carefully controlled vapor pressure conditions was largely eliminated in these measurements. The specimens used were sufficiently large to permit the setting up of moisture gradients across the sections during the process of drying. This combined with the oscillations in vapor pressure permit alternate desorption and adsorption to take place, thus tending to establish an intermediate moisture content equilibrium. The appreciable reduction in hysteresis obtained in this way is illustrated in figure 1 by the oscillating vapor pressure–desorption curve. The normal desorption and the adsorption curves shown in figure 1 were obtained by Seborg and Stamm (5) by using very small cross sections of wood suspended from quartz helical balances in thermostatically controlled (25° ±0.02°C.) tubes through which air humidified over saturated salt solutions was passed. These carefully controlled conditions tend to promote the maximum hysteresis effect. All the available drying data obtained under industrial control conditions on other softwood species also gave curves which fell within this hysteresis loop. The oscillating vapor pressure–desorption curve approaches more nearly the normal desorption curve at high relative vapor pressures and the adsorption curve at low relative vapor pressures. This would be expected on the basis of Urquhart and Williams' (8) explanation of the hysteresis loop. In the initial desorption the maximum number of the hydroxyl groups of the amylene oxide chains of cellulose are satisfied by water. When the material approaches the dry state these hydroxyl groups are drawn closer and closer together as a result of shrinkage, and they finally mutually satisfy each other. On adsorption part of these hydroxyl groups are not freed for water adsorption, thus accounting for the decreased moisture equilibrium values. Oscillating vapor pressure conditions at high relative vapor pressures hence have only a slight tendency to cause the hydroxyl groups of the cellulose mutually to satisfy each other, whereas this tendency becomes appreciable at low relative vapor pressures.

The dotted line in figure 1 connecting the origin with the saturation point represents the sorption conditions that would be attained if Henry's law were followed. This line is tangent at the origin to the curve for hysteresis-free sorption, showing that Henry's law is obeyed at infinitesimal concentrations.

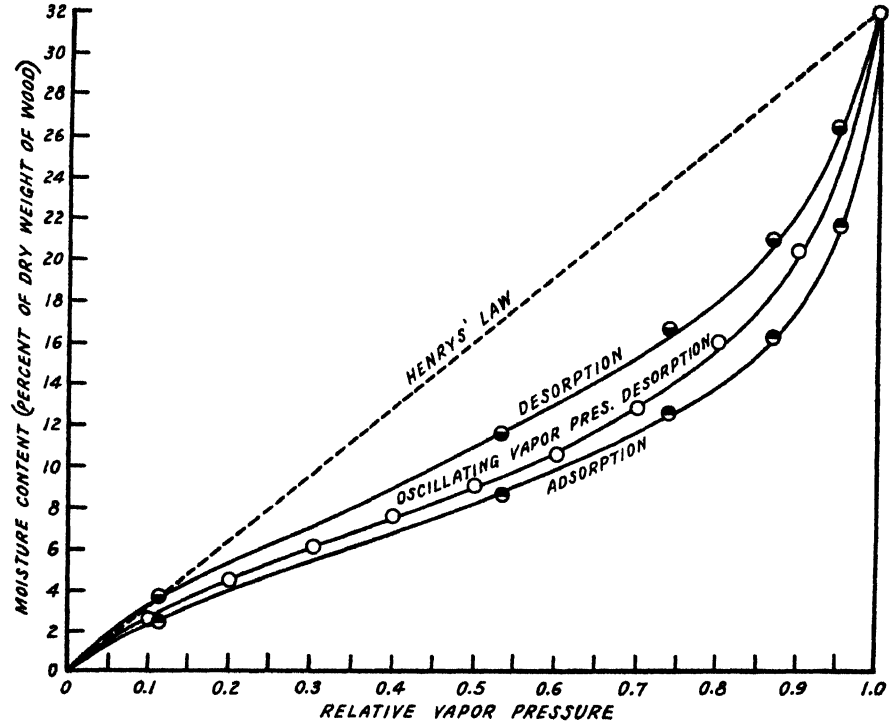

FIG. 1. MOISTURE CONTENT–RELATIVE VAPOR PRESSURE RELATIONSHIP FOR SITKA SPRUCE UNDER NORMAL DESORPTION AND ADSORPTION CONDITIONS AND UNDER OSCILLATING VAPOR PRESSURE DESORPTION CONDITIONS AT 25°C.

In figure 2 the moisture content–relative vapor pressure isotherms for Sitka spruce are plotted for 10°F. temperature intervals from room temperature to the boiling point of water. The changes in the fiber-saturation points (saturation moisture content) with temperature are given in figure 3. The fiber-saturation points change linearly with the temperature, increasing approximately 0.1 per cent for a decrease in temperature of 1°C.

In figure 4 are plotted the differential heats of swelling calculated with the aid of equation 2 from the data of figure 2 together with differential

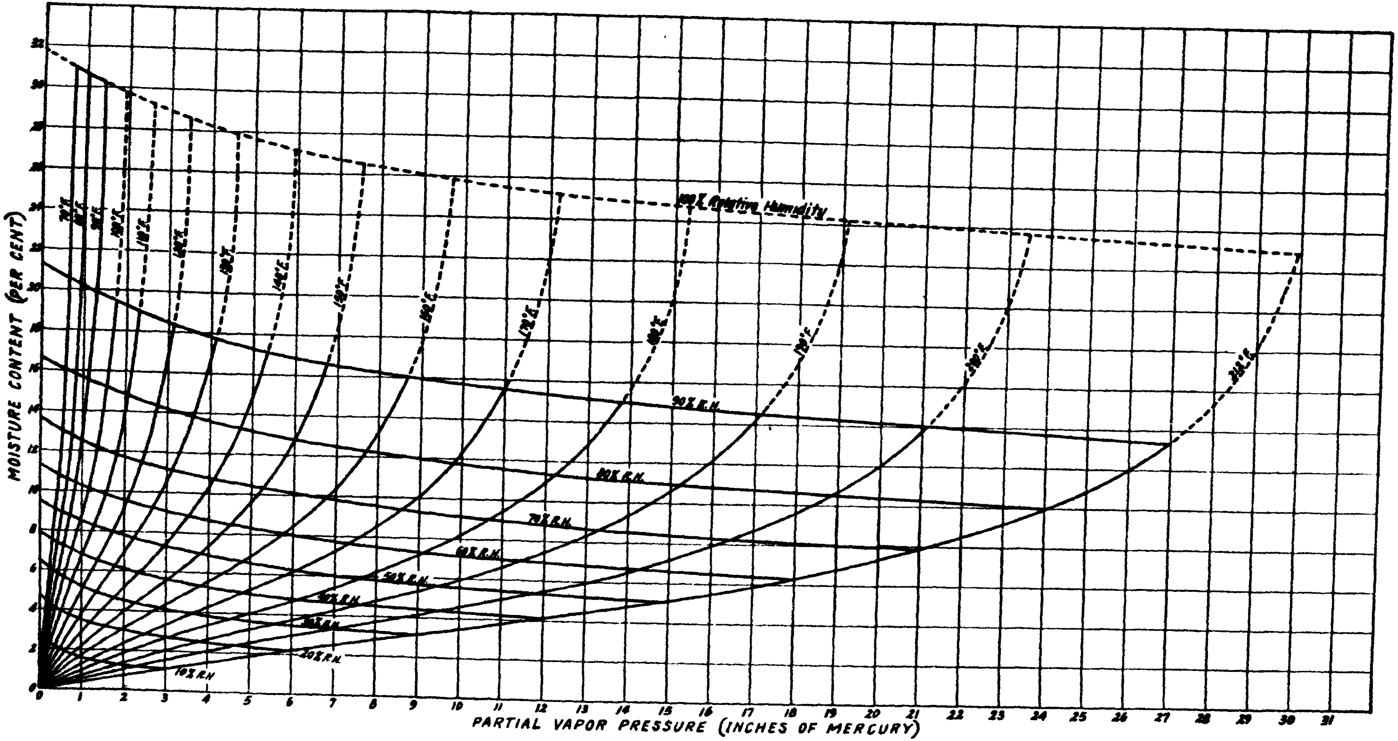

FIG. 2. THE MOISTURE CONTENT OF SITKA SPRUCE AT EQUILIBRIUM WITH VARIOUS TEMPERATURES, PARTIAL VAPOR PRESSURES, AND RELATIVE HUMIDITIES UNDER OSCILLATING VAPOR PRESSURE CONDITIONS

The solid lines in the curves are based on experimental data; the dotted parts of the lines are calculated heat of swelling obtained from the integral heat of swelling data of Volbehr (9). The 87.8°C. curve was calculated from the 200° and 180°F. isotherms, the 71.1°C. curve from the 200° and 120°F. isotherms, and the 54.4°C. curve from the 140° and 120°F. isotherms. The 0°C. curve is the experimental curve of Volbehr. Below 6 per cent moisture content the curves are all identical within experimental error. Above this moisture content the values of ΔH increase with a decrease in temperature. Volbehr's experimental values for pine are in complete accord with the calculated values given for Sitka spruce. The agreement between species is not surprising, as practically all softwoods have almost identical fiber-saturation points (7) and would be expected to have similar adsorptive powers.

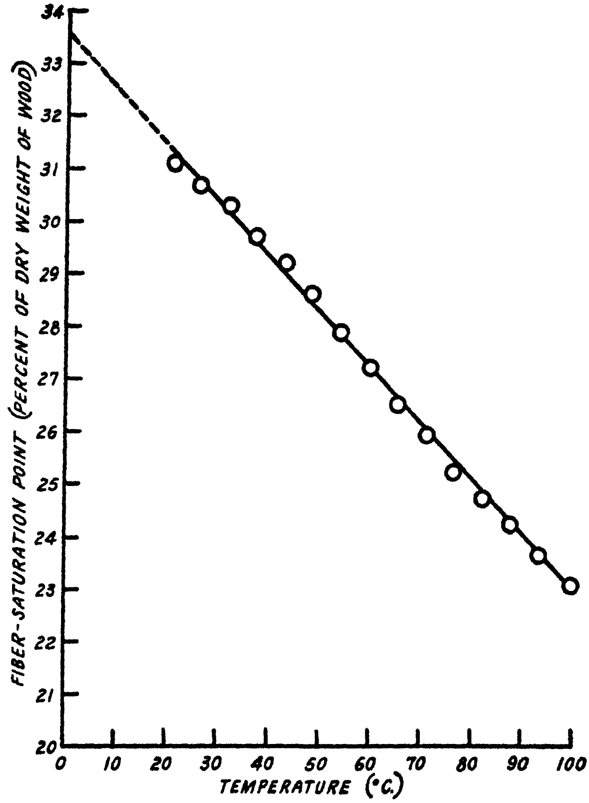

FIG. 3. CHANGE IN FIBER-SATURATION POINT WITH TEMPERATURE FOR SITKA SPRUCE

In figure 5 are plotted the isosteres, logarithm of vapor pressure against the reciprocal of the absolute temperature, for a number of different moisture content values from the data of figure 2. The linear isosteres at the

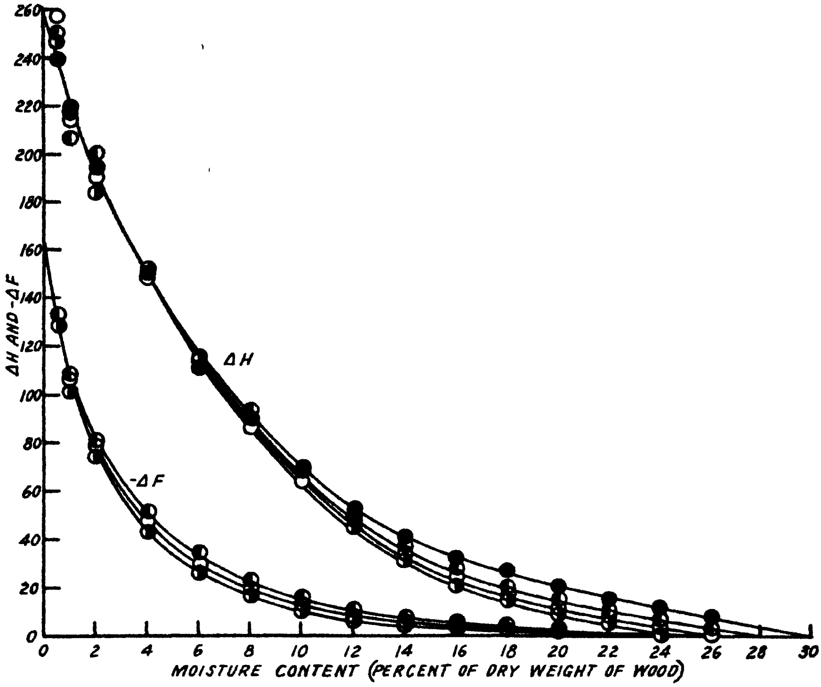

FIG. 4. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY CHANGE WITH MOISTURE CONTENT FOR SITKA SPRUCE

● Experimental curve of Volbehr at 0°C.
◐ Calculated curve of authors at 54.4°C.
○ Calculated curve of authors at 71.1°C.
◑ Calculated curve of authors at 87 8°C.

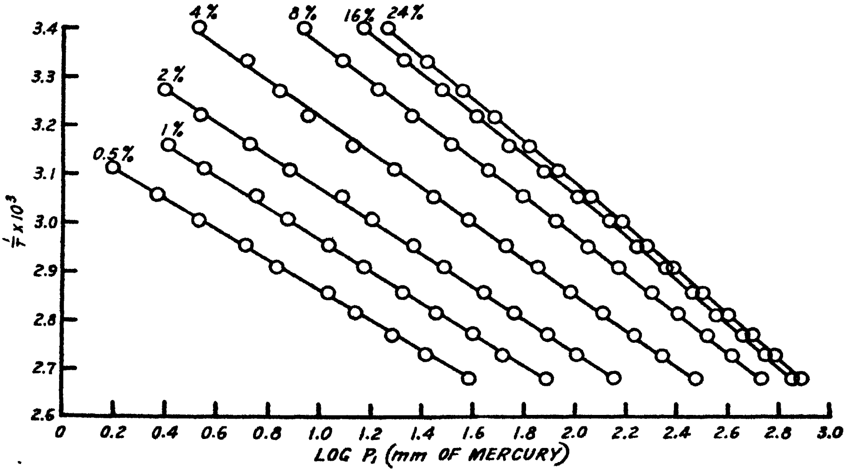

FIG. 5. LOGARITHM OF VAPOR PRESSURE–RECIPROCAL OF THE ABSOLUTE TEMPERATURE ISOSTERES FOR SITKA SPRUCE AT THE INDICATED MOISTURE-CONTENT VALUES

lower moisture content values indicate that the temperature coefficient of the heats of swelling is zero. The slight convex curvature of the isosteres at higher moisture contents indicates that the ΔH values increase slightly with a decrease in temperature. This agrees with ΔH curves in figure 4. The heat of swelling can also be calculated from these isosteres by taking the difference between the slope of any isostere and the saturation isostere thus:

$$\Delta H = -\frac{R}{M}\left(\frac{\mathrm{d}\ln P_1}{\mathrm{d}\frac{1}{T}} - \frac{\mathrm{d}\ln P_0}{\mathrm{d}\frac{1}{T}}\right) \tag{4}$$

The isosteres for the lowest moisture content values approach parallelism. This would be strictly true only if Henry's law were obeyed.

The changes in the free energy of swelling calculated with the aid of equation 1 are plotted in figure 4 together with the heat of swelling curves. These were calculated from the 190°, 160°, and 130°F. isotherms, respectively. The $-\Delta F$ values increase very slightly with a decrease in temperature.

In figure 6 are plotted the entropy change curves calculated with the aid of equation 3. They show that a definite entropy change accompanies swelling up to the fiber-saturation point. The entropy changes for the moisture content values below 6 per cent are unaffected by the temperature. At higher moisture content values there is a definite increase in the entropy change with a decrease in the temperature.

The ΔH, $-\Delta F$, and ΔS curves are all smooth curves which show no sign of a sharp transition between the bound or surface adsorbed water and the capillary condensed water or water held by van der Waals forces, although the ΔS curves show a slight inflection at low moisture content values. This is in keeping with the moisture content-relative vapor pressure curves which also lack a sharp discontinuity. The points of adsorption must thus vary in activity as in the case of a metal catalyst. The attractive force at the weakest of these adsorption points must be of the same order of magnitude as the van der Waals force exerted by the most active adsorption point at a distance of at least one molecular diameter from the surface. Such a gradual transition, with perhaps a slight overlapping, from surface-bound water to water held by the van der Waals forces has been recently illustrated in a diagrammatic manner by Sheppard and Newsome (6). It is also very similar to the two-phase adsorption theory of Pierce (4) who, however, believes that a dynamic equilibrium is set up over the whole sorption range between the surface-bound water and water held by van der Waals forces such that the fraction of the total water taken up that goes into the bound phase is proportional to the ratio of unoccupied true adsorption positions to the total number of adsorption positions. According to these conceptions the inflection point in the moisture content–relative vapor pressure curves corresponds approximately to the transition point between the surface-bound water and the water held by van der Waals forces. It is interesting to note from figure 2 that this inflection point occurs at a relative vapor pressure of about 0.30 for all of the temperatures. This relative vapor pressure further gives a capillary radius when applying Kelvin's equation for the relationship between meniscus curvature and vapor pressure that is only 2.3 times the molecular diameter. This is very near the limiting distance expected for primary molecular attraction, and should represent the limiting size of capillary in which capillary condensation can take place.

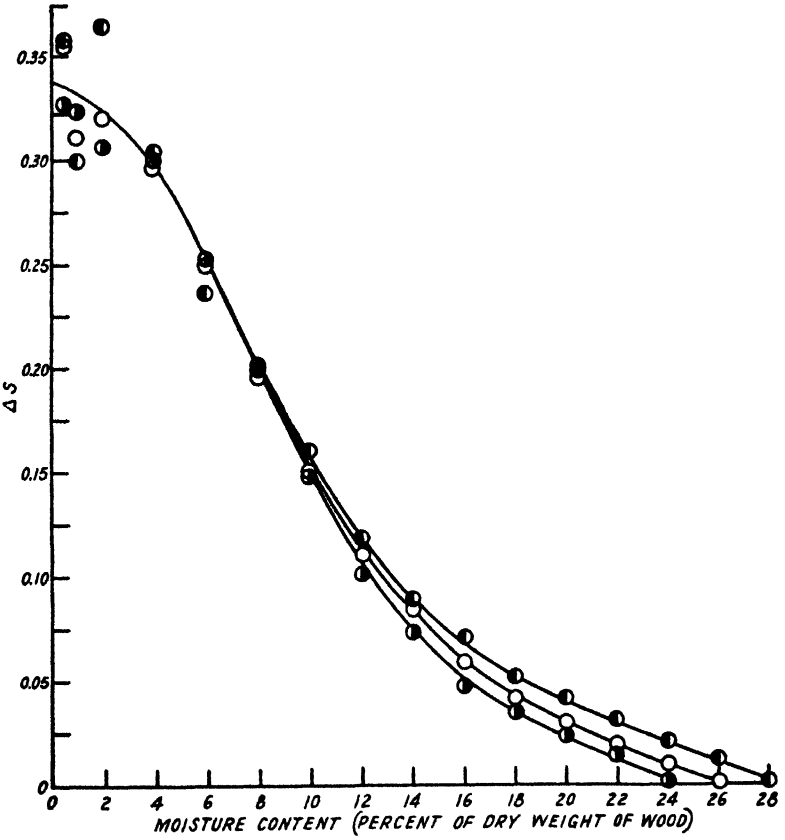

FIG. 6. CHANGES IN ENTROPY WITH CHANGES IN MOISTURE CONTENT OF SITKA SPRUCE

◐ 54.4°C. ○ 71.1°C. ◑ 87.8°C.

In figure 7 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for soda-boiled cotton calculated from the adsorption data of Ur-

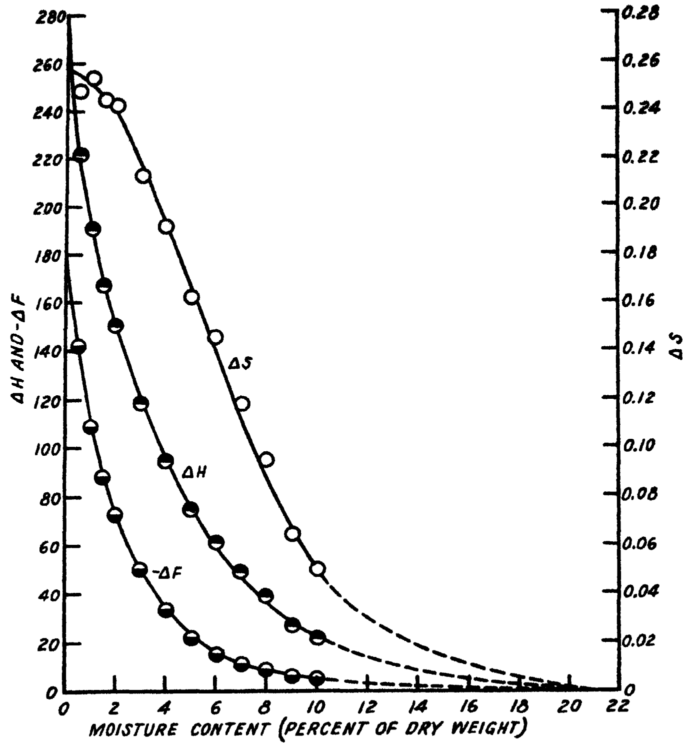

FIG. 7. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY AND ENTROPY CHANGES WITH MOISTURE CONTENT AT 50°C. FOR SODA-BOILED COTTON CALCULATED FROM THE DATA OF URQUHART AND WILLIAMS

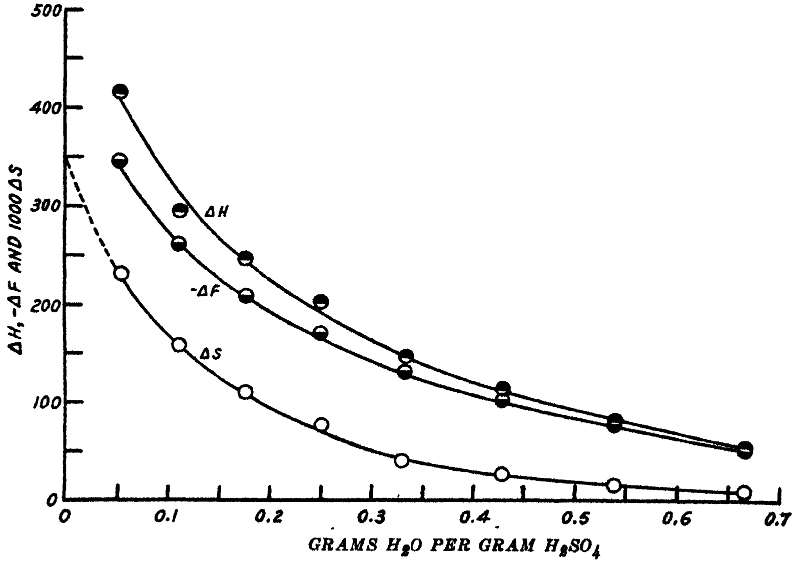

FIG. 8. HEAT OF SOLUTION AND FREE ENERGY AND ENTROPY CHANGES FOR SULFURIC ACID-WATER MIXTURES AT 50°C., CALCULATED FROM DATA TAKEN FROM THE INTERNATIONAL CRITICAL TABLES

quhart and Williams (8). The ΔH values were calculated from the 60° and 40°C. moisture content–relative vapor pressure isotherms and the $-\Delta F$ values from the 50°C. isotherm. It was not possible to correct for the effect of hysteresis; hence the values should be considered only approximations. All three curves are very similar, however, to those for wood. Urquhart and Williams (8) also give isosteres similar to those of figure 5. All of them, however, show a very slight convex upward curvature.

In figure 8 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for sulfuric acid–water mixtures calculated from data obtained from the International Critical Tables. As Katz (2) has pointed out, there is a close analogy between solution and swelling. Unfortunately, the data do not extend to moisture content values sufficiently low to determine if the ΔS curve has an inflection point.

TABLE 1

Thermodynamic constants for the swelling and solution of various materials in water expressed in gram-calories per gram of water added to an infinite amount of the material at the moisture content indicated in the subscripts

MATERIAL	SOURCE OF DATA	ΔH_0	ΔS_0	$\Delta H_{4.0}$	$-\Delta F_{4.0}$	$\Delta S_{4.0}$
Wood:						
Sitka spruce.........	Stamm and Loughborough	270	0.34	150	46	0.30
Pine..................	Volbehr (9)	260		150		
Cotton................	U. and W. (8)	280	0.26	95	33	0.19*
Cotton................	Katz (2)	390				
Starch........	Katz (2)	320				
Nuclein (from yeast)....	Katz (2)	200				
Casein...............	F. and L. (1)			166	70	0.35
Casein................	Katz (2)	200				
Agar-agar...............	F. and L. (1)			222	125	0.35
Keratin...............	F. and L. (1)			150	90	0.22
Sulfuric acid..............	International Critical Tables			440	365	0.23
Sulfuric acid...........	Katz (2)	550				

* No correction made for hysteresis effect.

Table 1 gives the initial heat of swelling or solution, the initial entropy change, and also the differential heat of swelling and free energy and entropy changes at 4 per cent moisture of a number of materials in water. Although the variation in ΔH and $-\Delta F$ values among the different materials is as great as five to ten times, the variation in ΔS values is less than twofold, showing that the non-reversible work of sorption is fairly constant for a wide variation of materials.

SUMMARY

1. Relative vapor pressure–moisture content desorption isotherms from room temperature to the boiling point of water have been determined for the system wood–water under conditions which minimize the hysteresis effect.

2. The fiber-saturation points decrease with an increase in temperature in a linear manner, the fiber-saturation point being reduced 0.1 per cent for each rise in temperature of 1°C.

3. Differential heats of swelling and free energy and entropy changes were calculated over the entire sorption range. All give smooth curves with zero values at the fiber-saturation point.

4. The nature of the curves with respect to the mechanism of sorption is discussed.

5. Comparisons are made between heats of swelling and free energy and entropy changes for the swelling and solution of various materials in water.

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ADSORPTION COMPRESSION ON CELLULOSE AND WOOD. I

Density Measurements in Benzene

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INTRODUCTION

The apparent density of an adsorbent material with a large extent of internal surface varies with the nature of the displaced medium used for making the measurements. Harkins and Ewing (9) attributed the phenomenon in the case of charcoal to varying degrees of adsorption compression of the displaced liquid in the capillary structure. They obtained the greatest densities in the most compressible liquids. The size of the molecules of the displaced liquid and the ratio of their surface tensions to viscosities showed no correlation with the densities. They concluded that the differences in the density values could not be due to differences in penetration. Lamb and Coolidge (13) calculated compressive force values as high as 37,000 atmospheres from their heats of adsorption measurements on charcoal, by assuming that all of the heat evolved is due to compression of the liquid. Cude and Hulett (5) made measurements of the density of charcoal in various liquids which they injected into the charcoal under pressure to facilitate penetration, and Howard and Hulett (10) made measurements in helium gas which they showed to be nonadsorbed on the charcoal. The helium gas gave quite similar values to those obtained in the various liquids, thus indicating that any adsorption compression taking place in the liquids would have to be much less than the values predicted by Lamb and Coolidge.

Davidson (6) determined the specific volume of cotton in helium gas, water, and several organic liquids. Non-polar organic liquids gave the highest values, the helium gas values were but slightly less, and the water values were still smaller. He concluded that the helium gas gives the true values and that the slightly higher values in the non-polar organic liquids are due to incomplete penetration, while the low values in water are due to adsorption compression. He calculated values for the average compression of the sorbed water of approximately 2000 atmospheres on the basis of the compression taking place entirely in the water. This assumption seems justified, especially in the case of cellulose, because of the fact that x-ray measurements show no change in the x-ray diagrams on swelling of the cellulose in water (11, 12).

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[1] Maintained at Madison, Wisconsin, by the Forest Service of the U. S. Department of Agriculture, in coöperation with the University of Wisconsin.

Similar measurements on wood have been made at the Forest Products Laboratory (16). Helium gas gave intermediate density values between those obtained in water and in non-polar organic liquids as in the case of Davidson's measurements, but the helium gas values were nearer to the water values than to the non-polar liquid values. In the light of more recent findings these helium gas values appear high. Measurements in this medium are now being repeated. A series of organic liquids gave the greatest density values in the most polar liquids which cause swelling and the lowest density values in the non-polar liquids which do not cause swelling. No relationship between the density values and the compressibilities of the liquids was obtained. Water, a slightly compressible liquid, gave the greatest density. These results for hydrophilic cellulose may appear to be in conflict with those of Harkins and Ewing (9) for hydrophobic carbon, but this is by no means the case. The internal surface of contact for non-swelling carbon is constant except for possible slight variations in penetration, while in the case of cellulose and wood, which are subject to swelling, it may vary from several hundredfold to a thousandfold. For example, the estimated internal swollen surface of cellulose and wood varies from 3×10^6 to 10^7 square centimeters per gram (14), while the coarse capillary surface of unswollen wood (total lumen area) varies from 1 to 5×10^3 square centimeter per gram. The extent of the surface on which compression can take place, rather than the magnitude of the compression per unit of surface, thus appears to be the prime factor in causing the variation in the density values of swelling solids obtained in different liquids.

Filby and Maass (7) have made measurements in helium gas of the density of cellulose with various amounts of adsorbed water present by an ingenious combined gas expansion and moisture sorption method. From the few measurements which they reported they drew several very far-reaching conclusions: First, that the compression takes place only within the first 8 to 10 per cent of moisture adsorbed; second, that a constant maximum compression is reached at moisture content values below about 4 per cent; and third, that the initial compression amounts to 0.6 cc. per gram of water adsorbed. An externally applied compressive force of about 100,000 atmospheres would be required to give this compression. The first two conclusions are not in harmony with moisture content–relative vapor pressure data or heats of swelling data (17). Vapor pressure depressions and differential heats of swelling are obtained at all moisture content values up to the fiber-saturation point, which varies from

15 to 35 per cent for the different fibrous materials. It thus seems unreasonable that the compression, which is a related property, should not be effective up to these higher moisture content values. Further, the moisture content–vapor pressure and the moisture content–entropy change data show inflection points at presumably the transition point between the bound and capillary held water, but they do not indicate a constancy of attractive force of all of the sorption points (17) as in the case of the data of Filby and Maass. The extremely high compression obtained by these investigators would require that the work of adhesion of cellulose and water be seven to eight times the work of cohesion of water. This, too, is at variance with other data. Bartell and Osterhof (2) and Bartell and Jennings (1) have shown from adhesion tension measurements that the work of adhesion for a solid wetted by water is but 1.00 to 1.05 times the work of cohesion of water. The work of adhesion of mercury and water according to Harkins (8) is only 1.25 times the work of cohesion of water.

Because of these irreconcilable results of Filby and Maass and the general unsettled opinions as to the magnitude of adsorption compression, the Forest Products Laboratory undertook this research with the hope of settling this point, which has considerable bearing on the general problem of sorption.

EXPERIMENTAL

The measurements of Davidson (6) show that the specific volume of cellulose determined in toluene is only a little over 1 per cent greater than in helium gas. The difference must be due entirely to incomplete penetration by the toluene, as toluene is practically a non-swelling liquid in which the compression can be only 0.01 to 0.001 of that in a swelling liquid. Such a small compression would be outside the range of experimental measurement. It further seemed reasonable to assume that the small amount of void structure of cellulose or wood inaccessible to benzene or toluene would be filled by the first few per cent of water added, so that density measurements in these liquids of cellulose or wood containing appreciable amounts of sorbed water should give results free from the error introduced by incomplete penetration. Only in the case of dry or relatively dry cellulose or wood should an error be introduced by making density measurements in a non-swelling liquid.

For these reasons the density measurements of cellulose and wood containing sorbed water were made in benzene, thus greatly simplifying the measurements and increasing their accuracy.

Benzene was chosen in preference to toluene for the measurements because it caused no measurable swelling of wood, whereas toluene caused a very slight swelling. Although water is very slightly soluble in benzene, only in the case where the moisture present exceeds the fiber-saturation point of cellulose or wood could the benzene become saturated because of the vapor pressure depression caused by the cellulose or wood. The error caused by using dry benzene for the measurements should hence be small and will be shown later to be entirely negligible. The benzene used was a chemically pure benzene, thoroughly dried over phosphorus pentoxide, and then distilled.

The adsorbent materials used were Sitka spruce and white spruce heartwood sawdust of 40 to 60 mesh, from which the extractives had been removed by extraction with a mixture of benzene and alcohol, cotton linters alpha-cellulose, a normal spruce sulfite pulp, and the same pulp beaten for 20 hours to a "highly hydrated" condition. Beaten pulp when dried by ordinary methods becomes hard and horny. The water was hence replaced by alcohol and the alcohol, in turn, replaced by ether and then the pulp dried from this latter solvent. By drying in this way practically normal porous texture is obtained, and the sealing up of voids is prevented.

The measurements were made in 50-cc. and 100-cc. pycnometer flasks brought to thermal equilibrium in a thermostatic water bath held at 30°C. ±0.02°C. The volume of the pycnometers was obtained from their weight filled with water, and the density of the benzene was determined. The pycnometers were then half filled with cellulose or wood (3 to 10 g.) that had been brought to moisture equilibrium in rooms controlled at 97, 90, 75, 65, and 30 per cent relative humidity and 80°F., or partially dried over calcium chloride, weighed, and covered with anhydrous benzene. The air was removed from the submerged fibrous materials by carefully applying a vacuum and releasing until no sign of air bubbles was obtained up to a vacuum which caused boiling of the cold benzene. Experience showed that the cellulose and the wood could be completely freed from air after a few hours treatment. After bringing the pycnometers containing the adsorbent, water and benzene to thermal equilibrium and volume in the thermostatic bath, they were rapidly weighed. The weights in general could be checked to 0.5 mg. The excess of benzene was then decanted off, and the materials dried at 105°C. to constant weight.

The compression of the water was calculated with the aid of the following equation:

$$C = \frac{\dfrac{w_w}{d_w} - \dfrac{W_b - (W - m_1)}{d_b}\,\dfrac{m_0}{D}}{m_0}$$

in which C is the decrease in volume due to compression in cubic centimeters per gram of dry adsorbent material, d_w the normal density of the water, d_b the density of the benzene, and D the true density of the adsorbent material, w_w the weight of sorbed water, m_0 the weight of the dry adsorbent material and m_1 the weight of the wet adsorbent material, W_b the weight of the pycnometer filled with benzene alone, and W the weight of the pycnometer filled with wet adsorbent material and benzene.

In figure 1 are plotted the apparent adsorption compressions for several cellulosic materials calculated on the basis of the density of the dry material as determined in benzene being the true density. The average densities of each of the materials determined in benzene are Sitka spruce 1.449, white spruce 1.459, sulfite pulp 1.529, beaten sulfite pulp 1.543, and cotton 1.549. The integral curves give the relationship between the total compression occurring in the water adsorbed on a gram of cellulosic material and the moisture content. The differential curves obtained by graphically determining the slope of the integral curves give the compression per gram of water adsorbed on an infinite amount of cellulosic material containing different amounts of water. The initial compressions, the compressions occurring when 1 g. of water is added to an infinite amount of dry material, are identical for all the cellulosic materials tested. The integral compressions increase up to maximum values which correspond to the maximum compressions calculated from the difference in the specific volume of the cellulosic material determined in water alone and in benzene. For example, the apparent specific volume of the normal sulfite pulp in water is 0.632 cc. and in benzene 0.653 cc. The difference, 0.021 cc., represents the decrease in volume due to compression of water. As an excess of water is present in these measurements, it is impossible to tell from them alone within what moisture content the compression takes place. The fact that

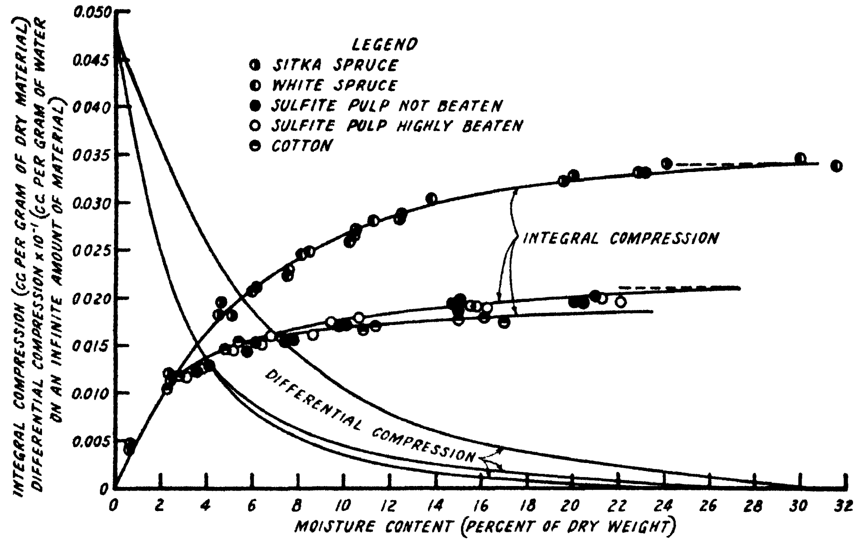

FIG. 1. APPARENT ADSORPTION COMPRESSIONS OF WATER ON VARIOUS CELLULOSIC MATERIALS AS DETERMINED IN BENZENE

the line representing this compression (dotted line in figure 1) becomes tangent to the integral compression curve at 27 per cent moisture content, which is the fiber-saturation point for this particular pulp, indicates that compression takes place up to the fiber-saturation point. It also indicates that the error introduced by neglecting the solubility of water in benzene in the compression measurements is negligible and that penetration is complete in the cellulosic material–water–benzene systems at high moisture contents.

It is of interest that not only the two similar species of wood give identical compression curves but that highly beaten and unbeaten pulp also give identical curves. This offers further proof of the fact that beating a pulp does not increase the surface available for the adsorption of water (4, 14, 15).

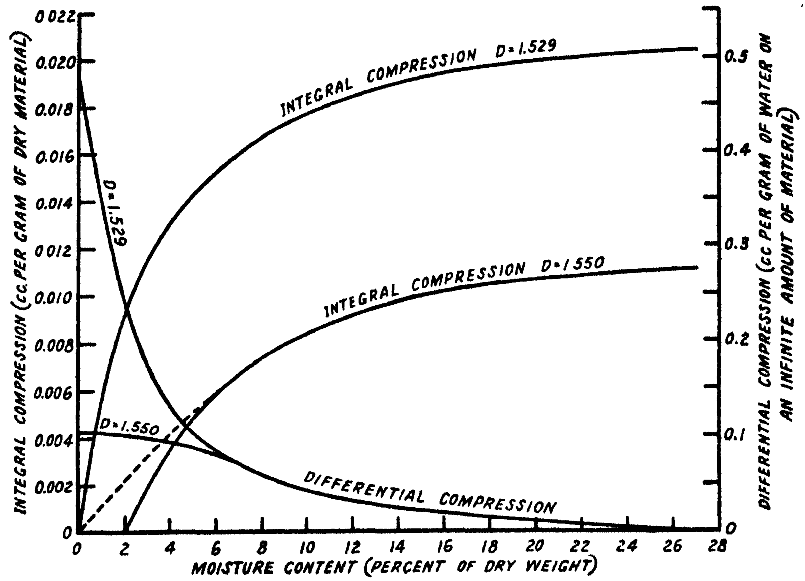

FIG. 2. EFFECT OF CHANGES IN THE VALUE OF THE ABSOLUTE DENSITY OF SULFITE PULP UPON THE CALCULATED ADSORPTION COMPRESSION

As was pointed out earlier, these compression values are liable to be too high because of incomplete penetration of the cellulosic materials by the benzene at low moisture content values. If, for example, the true density of the sulfite pulp were higher than the value determined in benzene, the compression would be appreciably decreased, as is shown in figure 2. The upper integral compression curve is the same curve as that plotted in figure 1, using 1.529 for the density, while the lower curve was obtained on the basis of the true density being 1.4 per cent higher, which is higher by practically the same amount that Davidson's values (6) determined in helium gas are higher than his values determined in toluene. These two curves are identical except for an additive shift of the ordinates. The lower curve does not pass through the origin, indicating in this case that no compression could take place below a moisture content of 2 per cent and that it would then suddenly become appreciable. Such a condition is ridiculous. The curve must pass through the origin without exhibiting an inflection point to avoid such a condition of reversal in compression. The dotted curve through the origin and tangent to the compression curve would avoid this difficulty. Assuming that the dotted curve represents the true conditions at low moisture content values, then the upper curve must be in error below 6 per cent moisture content, presumably because of incomplete penetration which would cause a reduced apparent compression.

The differential curves were obtained from both the upper curve and the lower curve with the dotted extension to the origin. They are identical down to a moisture content of 6 per cent, but deviate greatly below this point. The initial compression from the upper curve is 0.48 cc. per gram of water adsorbed on an infinite amount of dry pulp which corresponds, according to the extrapolation of the compression data of Bridgman (3), to an externally applied compressive force of over 100,000 atmospheres, while the lower curve gives an initial compression of only 0.105 cc., which corresponds to an externally applied compressive force of 3440 atmospheres. As this tremendous difference in the calculated compressive force results from a change of the value taken for the absolute density of the pulp substance of only 1.4 per cent, it is obvious that accurate values for this density must be known before even approximate values for the initial force of compression can be obtained.

The following analogy as well as other previously mentioned considerations, however, indicates that the latter value is perhaps a better estimate of this force than the former.

Katz (11) has pointed out the similarity between the sorption of water vapor by a solid and the mixing of sulfuric acid and water. In this latter case the difficulty of distinguishing whether changes in the specific volume of the system are due to differences in penetration or differences in compression become meaningless. The system sulfuric acid–water is hence an ideal one to examine from the standpoint of the compression phenomenon. In figure 3 the compression values for the system sulfuric acid–water are plotted on three different bases. The integral compression and molal compression curves were plotted from data for the density of various concentrations of sulfuric acid taken from the International Critical Tables. The differential curve was obtained by determining graphically the slope of the integral curve as before.

The compression occurring in this system is not entirely due to the compression of water, as in the case of adsorption by cellulose and wood, for part of the compression takes place in the sulfuric acid. This is demonstrated by the molal compression curve in which the compressions per unit volume of solution are plotted against the mole fraction. The compression increases practically linearly with an increase in the moisture content up to proportions slightly in excess of 1 mole of water to 1 mole of sulfuric acid. Compression presumably takes place in these proportions. When equal molal proportions of sulfuric acid and water are mixed the compression takes place in all of the solution. In any other proportions either part of the acid or part of the water is in excess and is not compressed. Concentrated sulfuric acid is only 0.73 as compressible as water per unit of volume at 166 kg. per cubic centimeter (International Critical Tables).

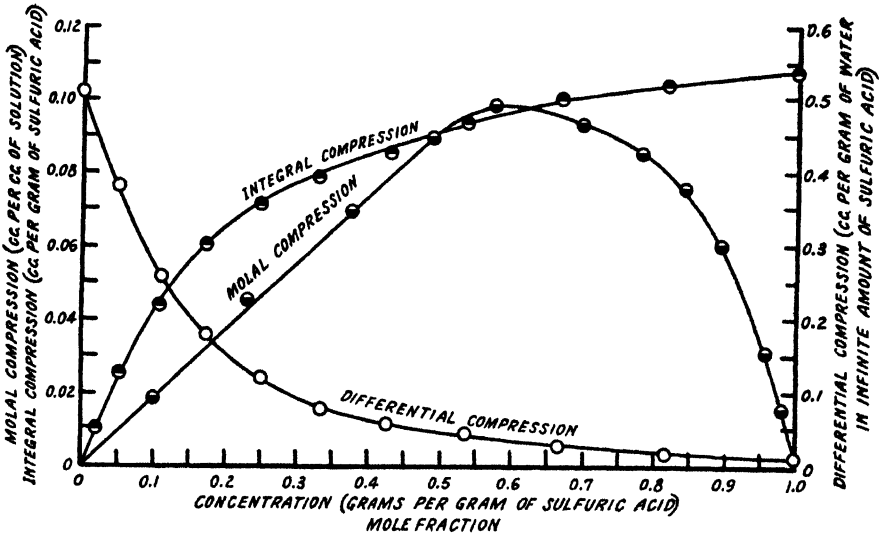

FIG. 3. COMPRESSION TAKING PLACE ON SOLUTION OF WATER IN SULFURIC ACID

If this ratio remains constant at all pressures, then the compression occurring in equal molal proportions per unit of pressure will be 3.21 times that in the contained amount of water alone. Thus the compression values given in the differential curve should be divided by 3.21 to obtain the compression that occurs in the water alone. The initial compression value would hence be 0.159 cc., rather than 0.51 cc. for the water. This compression, according to the data of Bridgman, would result from a compressive force of 6750 atmospheres. The differential compression of the water at equal molal proportions is 0.053 cc., which, in turn, would be obtained under a compressive force of 1450 atmospheres. These compressive forces are of the same order of magnitude as those obtained for the pulp by assuming that the true density of pulp is 1.4 per cent greater than the value determined in benzene. It thus seems probable that the densities of dry cellulosic materials as determined in benzene are slightly lower than the true densities, as was found by Davidson (6), and that Filby and Maass' compression values are too high. Measurements are now being made of the density of dry cellulosic materials in helium gas to confirm this point. These measurements together with thermodynamic considerations of compression will be given in a subsequent publication.

Although the data presented in this publication are insufficient to determine the magnitude of the adsorption compression of water on cellulosic materials at low moisture content values, they do give the true values at moisture contents above which penetration is complete and show quite definitely that compression continues to the fiber-saturation point. This is not in agreement with Filby and Maass' (7) contention that compression extends only to a moisture content of 8 to 10 per cent. Filby and Maass' own data, however, tend to disprove their contention, as the maximum compression calculated from their specific volumes in water and in helium gas alone correspond to the compression value of their extrapolated compression–moisture content curve at 22 per cent moisture content, which should be approximately equal to the fiber-saturation point of their cotton.

SUMMARY

1. The apparent adsorption compression of water on cellulosic materials has been determined in benzene.

2. The effect of small variations in the value used for the true density of the cellulosic material on the resulting compression is illustrated. Evidence indicating that the compressive force is of the order of a few thousand atmospheres rather than 100,000 atmospheres, is given.

3. It is demonstrated that actual adsorption compression values can be obtained by this method at higher moisture content values, and that adsorption compression extends to the fiber-saturation point.

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SOME PROPERTIES OF CELLULOSE ESTERS OF HOMOLOGOUS FATTY ACIDS

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In a previous paper (7) attention was drawn to the utility of working with homologous series of compounds in the effort to obtain quantitative characteristics of the solubilities of certain cellulose esters. In this paper the procedure is reversed, in so far that it is the cellulose esters themselves which here form the homologous series. The data recorded here for the most part apply to the triesters of cellulose. They are only strictly comparable on the assumption that the degree of polymerization of the cellulose remained the same through any given series, or, in other words, that the average molecular weight of the cellulose portion remained the same. In the series of compounds prepared in our own laboratories, where the same original cellulose material was used, we have reason to regard this as substantially the case, and the same may be regarded as equally probable for the material of other investigators cited. But while the comparisons in a *series* may be regarded as justified, it is not permissible to consider any given triester of investigator A as necessarily the same as that of investigator B. Identical in composition, they might differ considerably in average molecular weight.

With this reservation made, we can proceed to collate the data showing the progressive changes produced in cellulose esters as the molecular weight of the fatty acid is increased.

MEASUREMENTS OF PHYSICAL PROPERTIES

The melting points were determined by heating the sample in a glass capillary tube placed in a copper block.

The densities were determined by using methyl alcohol as the displacement liquid. Methyl alcohol wets the esters, especially the higher ones, much better than water and gives a higher density value than water. The esters were dried by evacuation at room temperature.

The data are shown in table 1 and figures 1 to 4.

The densities of the esters decrease regularly with increase in number of carbon atoms, corresponding to the behavior of the free acids (see table 2).

The melting points of the cellulose esters pass through a minimum at cellulose caprate, whereas the melting points of the normal fatty acids pass through a minimum at valeric acid, thus showing the influence of the cellulose residue.

There is no definite evidence of an alternation in the melting points of the esters with odd and even numbers of carbon atoms as is the case with the free acids. This effect, which is more pronounced for the lower acids, is apparently minimized by the presence of the cellulose residue—large in comparison to three hydrogen atoms. Since the alternating effect is attributed to differences in crystal structure (2), the presence of the cellulose residue should lower the degree of orientation and therefore reduce the magnitude of the alternation.

TABLE 1

Properties of cellulose triesters at 25°C.

ESTER	NO. OF CARBON ATOMS	DENSITY	MELTING POINT	PER CENT MOISTURE REGAIN		CONTACT ANGLE VS. WATER	WORK OF ADHESION VS. WATER
				50 per cent R.H.	100 per cent R.H.		
			degrees C.			*degrees*	*ergs*
(Cellulose)	0	1.618		5.6	18.8		
Acetate	2	1.377	Decomposes at 245	2.3	10.0	50	117
Propionate	3	1.268	239	1.3	4.4	78	87
Butyrate	4	1.178	183	0.7	3.5	84	79
Valerate	5	1.178	160	0.5	1.7	90	72
Caproate	6	1.110	87	0.3	0.9	93	68
Heptoate	7	1.081	97	0.2	0.8	100	59
Caprylate	8	1.058	85	0.1	0.9	99	61
Pelargonate	9	1.032	66	0.1	1.0	100	59
Caprate	10	1.026	64	0.3	1.5	100	59
Laurate	12	1.004	80	0.3	1.4	101	58
Myristate	14	0.991	87		1.5	104	55

The moisture regain apparently passes through a minimum near cellulose heptoate. The reason for this is not known. It appears that the moisture regain should continue to decrease with increase in number of carbon atoms in the side chains.

The contact angle against water steadily increases with increase in length of the hydrocarbon chain and approaches that of a long chain hydrocarbon—pure paraffin having an angle of 108° and work of adhesion of 50 ergs.

The method used for the determination of the contact angle, and therefore of adhesion tension or work of adhesion, was by measurement of the height of a drop of water placed on a horizontal surface of the solid (5).

The contact angle is given by the equation

$$h = a\sqrt{2}\sin\theta/2$$

where $a = \sqrt{\frac{2T}{g\rho}}$, h = height of drop in cm., T = surface tension of liquid, g = gravity, and ρ = density of liquid. The drop should be at least 1.5 cm. in diameter. Glass plates were coated uniformly with the various esters, from solutions of these in chloroform. The height of the drop was determined with a spherometer.

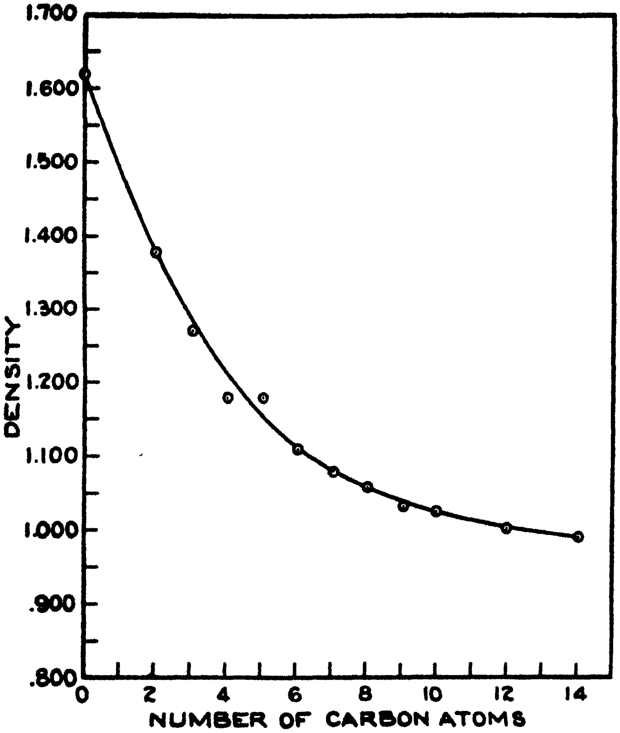

FIG. 1. DENSITY OF CELLULOSE TRIESTERS AT 25°C.

The work of adhesion is obtained from the contact angle θ by the formula

$$W = T_{LA}(1 - \cos\theta)$$

where T_{LA} is the surface tension, liquid to air.

It will be noticed that the values of the work of adhesion of water for the fatty acid esters of cellulose appear to fall steadily, finally approaching that of paraffin. On the other hand, A. H. Nietz (6) found for the fatty acids themselves a minimum value, in the neighborhood of twelve carbon atoms. Nietz discusses various molecular and thermodynamic explanations for this minimum, which are, however, unnecessary. The actual reason is the fact that the lower fatty acids (up to pentadecylic) have appreciable solubility in water, and therefore appreciable lowering of the surface tension T_{LA}. Consequently, while the contact angle θ rises more or less steadily (there is an alternating effect not found with the cellulose esters), the surface tension is at first nearly constant at a lowered value, then rises suddenly to be nearly equal to that of pure water above pentadecylic acid. Hence the minimum for the expression

$$W = T_{LA} (1 - \cos \theta)$$

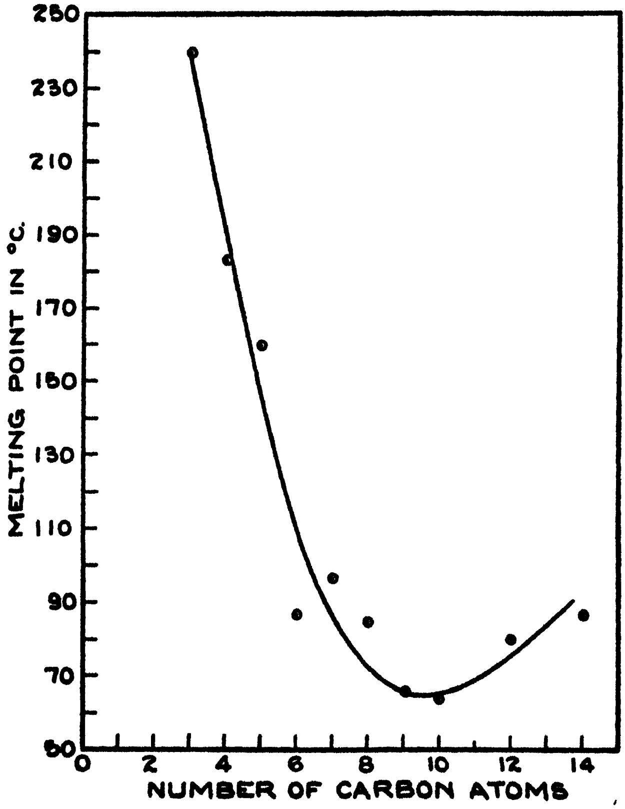

FIG. 2. MELTING POINT OF CELLULOSE TRIESTERS

SOLIDIFICATION AND MOLECULAR ORIENTATION

If the surface layers of molecules of these substances were completely oriented, as in a monomolecular film (4), then in accordance with Langmuir's theory of surface structure, we should expect to find either very high wetting (for the cellulose esters) or a very low (paraffin) value. The progression of values from high to low wettability indicates a—probably kinetic—effect of the chain length (in the case of the cellulose esters, side chain length) on the surface orientation on solidification.

In the case of the fatty acids themselves, Nietz found, using stearic acid, that the surface orientation on solidifying the melt depended decisively upon the medium in contact, i.e., the contiguous liquid or gas phase. High humidity or liquid water produced a surface of much higher adhesion tension, showing orientation of the polar groups to the water.

The increasing domination of the properties of the cellulose ester aggregate by the aliphatic side chains is well brought out in the studies of N. K. Adam (1) on the spreading of films of these substances on water, and in those of J. J. Trillat (9) on their x-ray spectroscopy. In figure 5 is reproduced Adam's data for the spreading of a number of fatty acid esters of cellulose.

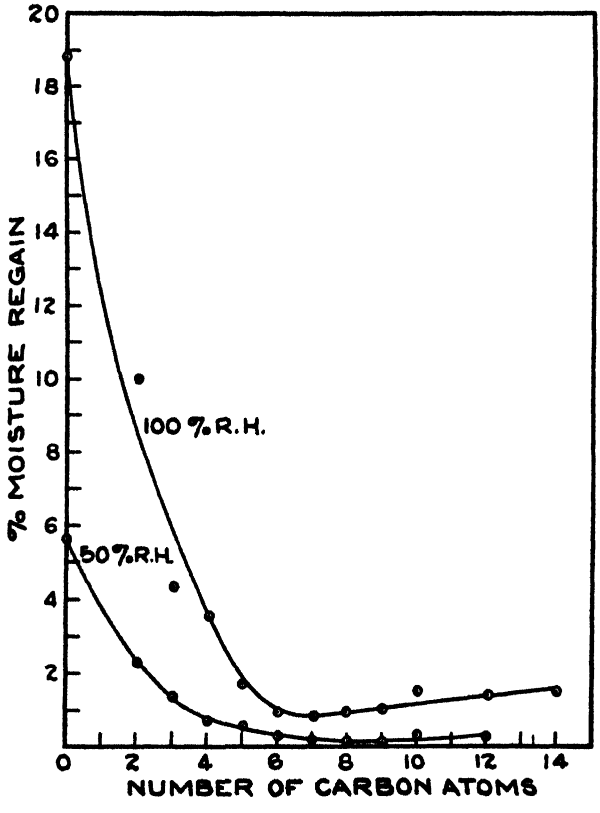

FIG. 3. MOISTURE REGAIN OF CELLULOSE TRIESTERS AT 25°C.

There is observable an increased "molecular" area covered as the length of the fatty acid chain increases (48 sq. A.U. for triacetate, ca. 78 sq. A.U. for tristearate). Adam concludes that "the hexose ring, lying *flat* on the surface of the water, occupies an area greater than that of the three eighteen carbon chains [also presumed to be flat on the water?]; and that lateral compression of the film allows some rearrangement of the hexose rings next the water, which form the base of the film, the *superstructure* of which no doubt *consists of the long chains arranged at a fairly steep angle to the surface.*[1] The lateral adhesion between the long 18-carbon chains is not sufficient to counteract the tendency of the hexose rings to lie flat."

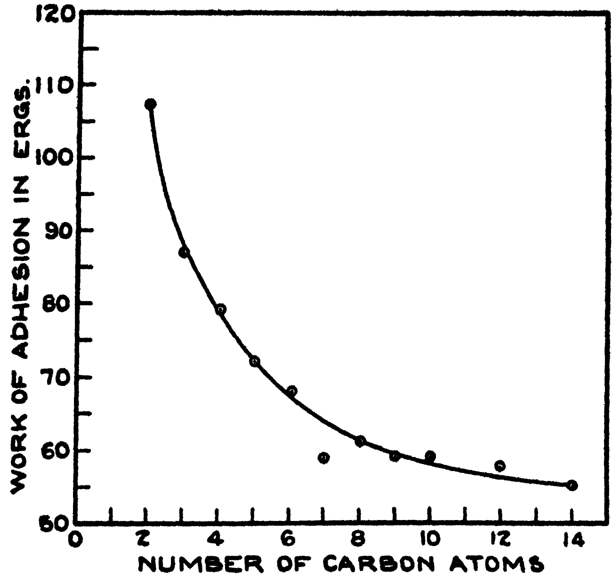

FIG. 4. WORK OF ADHESION OF CELLULOSE TRIESTERS AGAINST WATER

TABLE 2

Densities and melting points of normal fatty acids

ACID	DENSITY AT 20°C.	MELTING POINT
		degrees C.
Formic	1.220	8.4
Acetic	1 049	16 6
Propionic	0 992	−22.0
Butyric	0.959	−7 9
Valeric	0.942	−34.5
Caproic	0.929	−9.5
Heptylic	0.922	−10.0
Caprylic	0.910	16.0
Pelargonic	0.907	12.0
Capric	0.895	31 0
Lauric	0 883	48.0
Myristic	0.858	58.0
Stearic	0.847	69 3

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[1] Our italics.

These conclusions do not seem to us to be entirely tenable in the light either of general x-ray evidence on the structure of the cellulose macromolecule, or more specifically of Trillat's (9) results with the same series of fatty acid esters of cellulose whose properties were described here. This investigator found that the Debye-Scherrer transmission diagrams showed a structure greatly modified by the fixation of the long aliphatic chains. In brief, there were reproduced the diagrams of the fatty acids, or their metal salts, superposed on a (fading) cellulosic pattern. While the lower

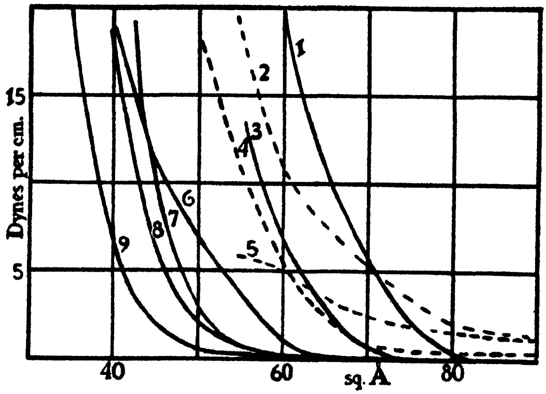

FIG. 5. FATTY ACID ESTERS OF CELLULOSE NOT FULLY SPREAD ON WATER

1. Tristearate
2. Tripropionate on sodium hydroxide
3. Dilaurate
4. 2½ Butyrate on sodium hydroxide
5. Triacetate on sodium hydroxide
6. 2½ Butyrate
7. Distearate
8. Tripropionate
9. Triacetate

N. K. Adam

TABLE 3

Tensile strength and total elongation of cellulose ester sheets

CELLULOSE ESTER	TENSILE STRENGTH	TOTAL ELONGATION IN PER CENT
	kg per mm ²	
Acetate	9–12	15–25
Propionate	6–7	10–15
Butyrate	5–6	8–10(?)
Valerate	4–5	18–25
Caproate	2 5	60
Pelargonate	3 5–4 0	20–30
Laurate	0 8–1 0	100–130
Stearate	0 5	140
Naphthenate	0 3	110

members (triacetate, tripropionate, tributyrate) have a definitely crystalline structure, the higher members show structure more and more mesomorphic.

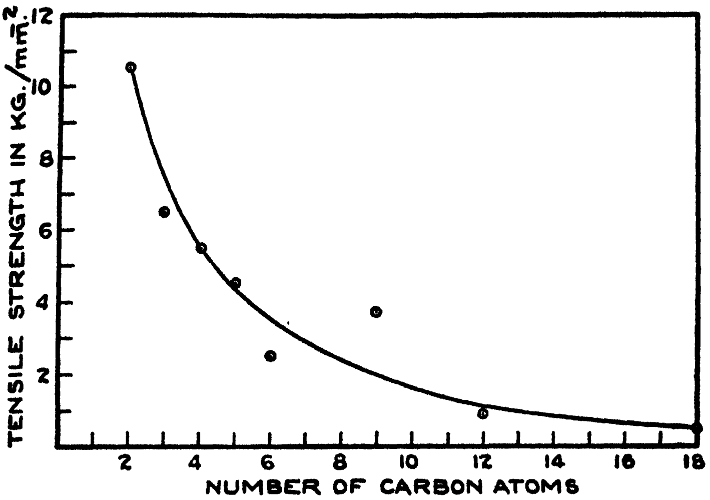

Fig. 6. Tensile Strength of Cellulose Ester Sheets

Hagedorn and Moeller

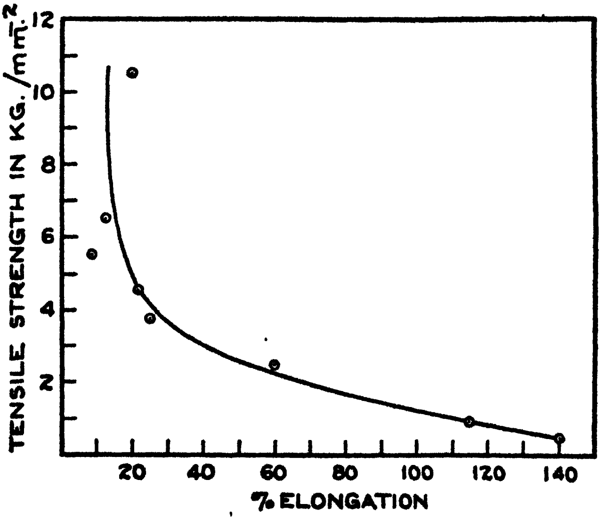

Fig. 7. Tensile Strength and Elongation of Different Cellulose Ester Sheets

Hagedorn and Moeller

Using the rotating crystal method for thin films of the esters compressed on glass sheets, it was found that in the degree that the side chain length increased, there appear reflexions of planes separated by intervals varying with the number of carbon atoms, planes parallel to the surface of the glass. "This indicates that the aliphatic chains, when their length is sufficient, orient themselves parallel to the direction of pressure, perpendicular to the plane of the support."

The aliphatic chains are placed perpendicularly, or nearly so, to the direction of the cellulose chain, that is, to the plane of the glucosan (or pyranose) ring. Further, there will be an alternation of direction of the two secondary substituents and the one primary.

In this way it is easy to see the mutual orientations as attractions of the cellulosic chains submerged and lost as the aliphatic chains increase in length. But also, this structure is difficultly compatible with that of Adam for the spreading on water. For the pyranose rings to lie flat on the water, there would have to be, not only a superstructure of hydrocarbon chains, but also an identical substructure extending down into the water. That does not seem very probable. Moreover, if this took place, the area in compression should remain substantially the same, *independent* of the length of the side chains.

For these reasons it seems more probable that the main valence chain must lie either edgewise or very much tilted on the water surface.

This progressive submergence of the cellulose skeleton by an adipose carcass is again brought out in the figures for elasticity and mechanical strength.

The tensile strength and total elongation at the breaking point of cellulose triesters are shown in table 3, and figures 6 and 7 as determined by Hagedorn and Moeller (3). The tensile strength decreases with increase in the number of carbon atoms in the side chain and the total elongation increases.

SOLUBILITY

The solubility of the higher fatty acid esters of cellulose has been discussed already by G. S. Whitby (10) at a previous symposium. He concluded that they were less polar than cellulose acetate, because of the longer hydrocarbon residues. But this does not seem a necessary conclusion, since according to Smyth (8) the polar moment need not change with length of chain. We do not propose to discuss this subject further here, beyond saying that the solubilities of the series of homologous triesters of cellulose do not support a theory of solubility based solely, or even mainly, on polarity and polar moment.

SUMMARY

A study has been made of the physical properties of a series of triesters of homologous fatty acids, from the acetate to the stearate. It shows the

"cellulose" character being progressively submerged as the length of the side chain is increased. The structure of the solids is interpreted from x-ray data and from spreading and wetting experiments.

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THE MOLECULAR WEIGHTS OF CELLULOSE AND CELLULOSE DERIVATIVES[1]

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INTRODUCTION

The nature of the solutions of the lyophilic colloids has long been a favorite subject for investigation by colloid chemists. Evidence has gradually accumulated from many sources to show that the well-known typical lyophilic colloids such as the proteins, rubber, gutta percha, starch, cellulose, and other polysaccharides and their derivatives, are polymeric materials of high molecular weight (45). In recent years a large number of synthetic high polymers possessing also the properties of lyophilic colloids have been prepared and carefully studied, particularly in the laboratories of Staudinger (55) and of Carothers (9). Many of the high polymers, both synthetic and natural, are now recognized to be "linear polymers;" i.e., the molecule is a single chain of recurring structural units bound together by primary valences. When, as is sometimes the case, the number of recurring groups in a molecule attains the magnitude of hundreds, it is indeed a giant or "macro" molecule. In many cases there is good reason to believe that these macromolecular substances are dispersed in solution to the individual molecule, and to a considerable degree the physical and colloidal properties of the solutions appear to be determined by the size and shape of the molecule. A substantial part of our understanding of the lyophilic colloids has come out of the study of the synthetic high polymers, which constitute excellent models for their better-known, naturally occurring prototypes.

A problem of fundamental importance in the interpretation of the behavior of macromolecular materials is the determination of their molecular weights. Numerous efforts have been made to employ the various colligative properties of solutions in accordance with classical methods for determining molecular weights, but the results have frequently been uncertain or inconclusive. Whenever the molecular weight exceeds a few thousand, the change in freezing point, boiling point, or vapor pressure is too small to be measurable with sufficient precision at the low concentrations necessary for satisfactory molecular weight determinations. Many of the values in the literature obtained by these methods for the naturally occurring high polymers and their derivatives are undoubtedly erroneous for one reason or another. A number of investigators have made limited use of osmotic pressure measurements, but the most comprehensive and conclusive work hitherto carried out on the problem is without question that of Svedberg and his associates for the proteins, using the Svedberg ultracentrifuge (58). Although these investigations have demonstrated the superiority of the ultracentrifuge over other methods, relatively little application of the method has yet been made to high polymers other than the proteins, partly because there are only two laboratories possessing the necessary equipment. The sum total of data obtained by other methods for proteins as well as other macromolecular substances is relatively meager, and the individual items are difficult to assess. In spite of this fact, it has become clear that protein solutions, at least for the cases that have been carefully studied, differ from most other macromolecular solutions in that the dissolved protein molecule is approximately spherical in form, whereas for other high polymers the solute unit is highly elongated. The difference is particularly strikingly manifested by the marked difference in viscosity characteristics, dilute protein solutions commonly having viscosities relatively independent of the molecular weight and in approximate agreement with Einstein's equation for spherical particles. On the other hand, the viscosities of most other macromolecular materials are very sensitive to molecular weight differences and are much greater than would be the case for spherical molecules (33).

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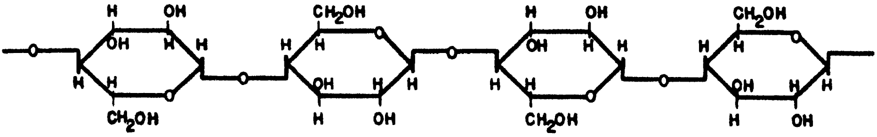
[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14-16, 1934.

Communication No. 144 from the Experimental Station. Second paper in the series on The Molecular Weight of Linear Macromolecules by Ultracentrifugal Analysis. The first paper appeared in J. Am. Chem. Soc. **55**, 4319 (1933).

The theory for the influence of highly elongated, perhaps flexible, molecules upon the free energy of a solvent has not yet been worked out, and it is therefore not known how far conventional methods for estimating molecular weights are applicable to polymers of the high-viscosity type. Having recently shown, however, that for one such case the molecular weight can be correctly determined with the ultracentrifuge (34), and taking into account the experimental efficacy of the instrument, we believe that it provides the most reliable and most effective method now known for estimating the molecular weights, in solution, of linear macromolecules of all kinds. We have accordingly selected this method of study for what we hope will eventually be a comprehensive investigation of cellulose and its derivatives.

Cellulose and its derivatives represent, next to the proteins, the most thoroughly studied class of high polymers and typify the high-viscosity group. For theoretical investigations concerning the nature of lyophilic colloids and their solutions, cellulose and its derivatives are particularly valuable. As will be seen, in certain cases they permit chemical conversions with little if any change in the length of the molecule. They offer several chemically related series of derivatives of considerable chemical stability for comparative studies. Many of them are soluble in a wide variety of solvents and permit avoidance of the ionic complications so characteristic of protein solutions. The molecular weight may be varied at will over very wide limits without a detectable change in chemical composition. Finally, x-ray crystal analysis has provided an unusual amount of valuable correlative information concerning the solid forms of cellulose and its derivatives.

It is now very generally agreed that the cellulose molecule is a long chain of anhydroglucose residues linked together by 1,4 glucosidic oxygen (reference 45, p. 91), in accordance with the following scheme:



On each glucose residue in the chain there are three hydroxyl groups which react with suitable reagents to give the various cellulose derivatives. Presumably, on one end of the chain the terminal glucose residue possesses four alcoholic hydroxyl groups, and at the opposite end there is a hemiacetal group. The length of the chain may vary within wide limits, probably being very long in native cellulose and passing through all intermediate lengths, as depolymerization occurs by breaking the oxygen links, until the final product is glucose. Whether the chains of native cellulose are uniform in length is not known, but in all probability, the length (or molecular weight) of degraded celluloses and derivatives is never uniform. This is a general characteristic of high polymers. Usually, therefore, when reference is made to chain length or molecular weight, an average value is meant. When comparing various celluloses and derivatives with respect to their molecular lengths, it is useful to specify the "degree of polymerization" (D.P.), by which is meant the number of glucose residues per molecule. For many years, industrial chemists interested in products manufactured from cellulose have assumed in a rather vague way that molecular "degradation" (without specification as to its chemical nature) of cellulose and its derivatives leads to reduction of the relative viscosity of their solutions (4, 48). As will be discussed in more detail below, it now appears that the viscosity characteristics of dilute solutions in good solvents are primarily determined by the degree of polymerization.

PREVIOUS INVESTIGATIONS OF THE MOLECULAR WEIGHT OF CELLULOSE AND CELLULOSE DERIVATIVES

Every method for the estimation of the molecular weight of macromolecules that we are aware of has been applied to cellulose and its derivatives. In a number of investigations, particularly the earlier ones in which freezing point or boiling point methods were usually used, values were obtained ranging from a few hundred to a few thousand (3, 5, 8, 29, 32, 46). In many cases later work failed to confirm these results, and in the light of present knowledge, it may be assumed either that the experimental technic was faulty (2, 17, 22, 44; 55, p. 453), or that the cellulosic materials were far more degraded than was suspected. Calculations of molecular weights by means of Einstein's equation for the diffusion coefficient of spherical molecules (24, 61) are now realized to be invalid, because the diffusion of cellulose and cellulose derivatives does not obey Fick's law and the solute particles are non-spherical (27, 38). On the basis of the breadth of the lines in the x-ray diffraction pattern, Mark (reference 42, pp. 163, 197) has inferred that the length of the crystallite in native ramie cellulose is about 600 A.U. Assuming that the length of the cellulose molecule is not longer than the length of the crystallite, and taking into account data from other sources, he has concluded that the molecule probably contains one hundred and fifty to two hundred glucose residues. Although this is an interesting speculation, it is admittedly not the only possible interpretation of the x-ray observations.

The most significant results hitherto made public have been obtained by means of osmotic pressure measurements, ultracentrifugal analysis, end-group determinations, and viscosity measurements. Even with these methods, there are gross discrepancies in the results, and there is not, as yet, general agreement as to which results are correct. The principal data are summarized in tables 1, 2, and 3.

In addition to molecular weights, the tables summarize the available data concerning the viscosity characteristics, in order to reveal to what extent a quantitative relationship exists between molecular weight and viscosity. Since the viscosity characteristics were not expressed by the various investigators in a uniform manner, the data were reduced to a common basis for comparative purposes by calculating $[\eta]$ defined by the expression[2]

$$[\eta] = \underset{c \to 0}{\text{lim.}} \left(\frac{\eta_r - 1}{c} \right)$$

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[2] For more detailed discussion of the advantages of comparing viscosities in infinitely dilute solutions, see references 36, 45 (p. 175), and 55 (p. 56).

where η_r is the viscosity of the solution relative to that of the solvent, and c is the concentration in grams per 100 cc. of solution. Extrapolation to zero concentration was made by means of Fikentscher's equation (14, 37). As Staudinger has shown, $[\eta]$ is directly proportional to the molecular weight for linear molecules of considerable length.[3]

Osmotic pressure results

Examination of table 1 shows that with a single exception the molecular weights of the cellulose ethers and esters as determined by the osmotic pressure method fall in the range 15,000 to 204,000, with most of the values falling between 25,000 and 100,000. In most cases the materials were commercial products or fractions thereof. The outstanding discrepancy is provided by the results of Hess and Ulmann (31) for Hess's crystalline cellulose triacetate II ("biosan acetate") by a modification of the method of Frazer and Patrick (15), in which the vapor phase serves as membrane. Inasmuch, however, as the authors report several quite unusual effects, such as a greater vapor pressure for a solution than for the solvent (60) and a remarkable reversible depolymerization of the triacetate, for which there are at present no generally accepted interpretations, the results cannot for the time being be considered as conclusive. In addition, Hess's crystalline triacetate does not display the properties characteristic of high polymers (e.g., large value of $[\eta]$, swelling behavior, and film-forming capacity) and is undoubtedly a relatively low molecular weight degradation product corresponding to a cellodextrin acetate (2, 16, 17, 19, 23, 44; 55, p. 460).

An important fact brought out by the osmotic pressure investigations is the non-uniformity of the cellulose derivatives with respect to molecular weight. The fractionation studies of Duclaux and Wollman (13) and of Medvedev (43) for cellulose nitrate, of Herzog and Deripasko (25) and of

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[3] In view of the increasing recognition of the value of characterizing the viscosity of solutions of macromolecular materials by the quantity $[\eta]$, there would be considerable advantage if investigators in this field could agree upon a suitable name for the quantity. In analogy to specific conductivity, specific volume, specific refraction, specific rotation, and the like, "specific viscosity" would serve very well. Unfortunately, the expression is already in use with two different meanings. It has long been used by Duclaux (10, 12) in referring to the constant k in Arrhenius's logarithmic equation ($\log \eta_r = kc$). Berl (4) refers to k as the "specific viscosity constant." If natural logarithms are used, $k = [\eta]$ for infinitely dilute solutions. Staudinger later adopted the term, "specific viscosity," for the quantity $\eta_r - 1$, but proposed no name for the more useful quantity, $[\eta]$. In passing, it may be pointed out that Staudinger's expression η_{sp}/c is equal to our quantity $[\eta]$ multiplied by one-tenth the weight of the structural unit of the particular linear polymer to which it refers, e.g., $\eta_{sp}/c = 162[\eta]/10$ for cellulose, the difference being due to the fact that Staudinger's concentrations are expressed in molarity with respect to the structural unit.

TABLE 1

Molecular weights of cellulose derivatives from osmotic pressures

CELLULOSE DERIVATIVE	MOLECULAR WEIGHT	D. P.	[η]	D. P./[η]	AUTHOR AND REFERENCE
Nitrocellulose	51,000	200			Duclaux and Wollman (12)
Nitrocellulose	21,000 to 70,000	80 to 270	1 5 to 3.1	50 to 100	Duclaux and Wollman (13)
Nitrocellulose	13,000 to 50,000	50 to 200	0 5 to 2.4	50 to 100	Duclaux and Nodzu (11)
Nitrocellulose	7,000 to 50,000	25 to 190	0 3 to 2 8	70 to 100	Grard (21)
Nitrocellulose	19,000 to 204,000	70 to 770	0 5 to 5.2	130 to 165	Buchner and Steutel (7)
Nitrocellulose	25,000 to 75,000	100 to 280	1 4 to 2 1	70 to 160	Medvedev (43)
Cellulose acetate	21,000 to 64,000	80 to 250	0 9 to 2.3	93 to 108	Herzog and Deripasko (25)
Cellulose acetate	20,000 to 152,000	110 to 600	1.0 to 2 3*	120 to 260	Herzog and Herz (26)
Cellulose acetate	23,000 to 34,000	90 to 130	1 2 to 2 1	55 to 85	Grard (20)
Cellulose acetate	33,000 to 45,000	130 to 180	0 9 to 1 8	80 to 145	Buchner and Samwel (6)
Cellodextrin acetate	576 to ∞				Hess and Ulmann (31)
Benzylcellulose	29,000	84			Herzog and Spurlin (28)
Ethylcellulose	14,000 to 63,000	60 to 270	0 7 to 3.4	35 to 90	Okamura (47)

* These viscosity measurements were made by ourselves.

Herzog and Herz (26) for cellulose acetate, and of Okamura (47) for ethylcellulose (see table 1) all agree in showing that the original materials contained a mixture of molecules of different weight. Numerous investigators have in other ways also demonstrated the heterogeneity of cellulosic products (39, 40, 49, 50).

The accuracy of the results, so far as revealed by internal evidence, varies somewhat for the different investigations. In most cases the ratio of pressure to concentration increases with concentration, i.e., the molecular weight apparently decreases with increasing concentration, and there is some question concerning the correctness of the extrapolation to zero concentration, particularly when the concentrations used were 1 per cent or more (6, 7, 20, 21). In other cases, where an effort was made to use low concentrations (25, 26), there was considerable irregularity in the resulting molecular weights. Notwithstanding, the values obtained are perhaps of the right order of magnitude.

Ultracentrifugal analysis

The data obtained from osmotic pressure measurements all refer to cellulose derivatives and leave the question of the molecular weight of cellulose itself entirely open. The only effective solvent for cellulose with a limited degrading action is Schweitzer's reagent, commonly referred to as cuprammonium solvent, but its complexity precludes its usefulness for osmotic pressure measurements. The molecular weight of cellulose dissolved in cuprammonium solvent has however been investigated by means of the ultracentrifuge by Stamm (54) and by ourselves (35). With respect to sedimentation equilibrium, the ultracentrifuge method is in basic theory similar to the osmotic pressure method as mentioned above. An important advantage, however, of the ultracentrifugal method is the fact that it yields information concerning the homogeneity of the sample being studied.

By the sedimentation equilibrium method, as recorded in table 2, Stamm found the molecular weight of the cellulose–copper complex formed in cuprammonium solvent,[4] and calculated cellulose molecular weights therefrom, on the assumption of one atom of copper per glucose residue. For a cotton-linters alpha-cellulose he obtained an average value of 56,000 for the copper complex or 40,000 on a copper-free basis, with no evidence for appreciable non-uniformity. Approximately the same value was obtained by the sedimentation velocity method. Wood celluloses of various sources were, on the other hand, found to be non-uniform, containing more or less relatively low molecular weight material in addition to various amounts of the constituent characteristic of cotton cellulose and a second constituent with a molecular weight of about 20,000 on a copper-free basis.

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[4] Strictly speaking, Stamm's method of calculating his results does not yield an exact value of the molecular weight of the cellulose–copper complex because of the difference between the specific volumes of the cellulose–copper complex and of cellulose.

As reported last year (35), we were unable to confirm Stamm's results and obtained a much larger value for the same cotton cellulose: 300,000 for the cellulose–copper complex or about 220,000 on a copper-free basis, as calculated by Stamm's method. Even degraded and regenerated celluloses gave values of 100,000 and greater. Although it is not certain, we believe that degradation inadvertently occurred during Stamm's measurements and, perhaps, that sedimentation equilibrium was not attained. On the basis of our investigation of a synthetic high polymer of known molecular weight, the results obtained by the sedimentation velocity method are of doubtful reliability as absolute values (34).

End-group determinations

Molecular weights by osmotic pressure and ultracentrifuge methods depend upon the state of dispersion of the solute in a solvent and are affected by association and solvation, with the consequence that the values so obtained may not correspond to the true molecular weight in the ordinary sense of the term. In contrast, the end-group method is independent of the laws of solutions, but depends upon knowledge concerning the chemical structure of the substance being studied. In principle, it is simply necessary to determine by suitable analytical means the proportion of glucose residues showing some chemical property characteristic of a terminal residue, from which the average number of glucose residues per molecule may be estimated. Two types of end-group determination may be used for cellulose or derivatives: one depending upon the terminal hemiacetal group, the other depending upon the terminal tetrahydroxyglucose residue.

The so-called copper number measures the reducing power of cellulose and presumably is due, at least in part, to the hemiacetal groups. The determination, unfortunately, is very sensitive to the conditions of experimentation, and the calculated molecular weights can scarcely be considered reliable (42, p. 192; 55, p. 491).

Bergmann and Machemer (2) developed an iodometric method for determining the hemiacetal content of cellodextrin acetates and used it in estimating molecular weights (see data of table 3). Unfortunately, the authors give no viscosity or other independent data indicative of the state of degradation of the products. In the discussion at the symposium of the Faraday Society, Machemer (41) reported that the iodometric method and the Haworth and Machemer method, involving the nonreducing end group, gave concordant results for cellodextrins with molecular weights in the range of 3000, but admitted that end-group determinations are not satisfactory for high-viscosity cellulosic products. Staudinger (reference 55, pp. 463, 491) was not able to obtain consistent results with this method for celluloses in any case, and only for highly

TABLE 2

Molecular weights of celluloses in cuprammonium by ultracentrifugal analysis

CELLULOSE	METHOD	MOLECULAR WEIGHT (CELLULOSE-Cu)	D P.	[η]	D.P /[η]	AUTHOR AND REFERENCE
Cotton celluloses	Sedimentation equilibrium	56,000	250	4 33	58	Stamm (54)
	Sedimentation velocity	56,000 + f*		4 15		
	Sedimentation velocity	56,000 + ff*		2 79		
Wood celluloses	Sedimentation velocity	2A† + 1B + ff		3 65		
	Sedimentation velocity	1A + 3B + ff		2 63		
Cotton celluloses	Sedimentation equilibrium	300,000	1300	5 05	260	Kraemer and Lansing (35)
	Sedimentation equilibrium	200,000	890	3 40	260	
	Sedimentation equilibrium	110,000	490	1 83	270	

* f indicates a small amount and ff indicates a considerable amount of a fine fraction of relatively low molecular weight.

† A represents a component with a molecular weight of 56,000, and B represents a component with a molecular weight of 28,000.

TABLE 3

Molecular weights by end-group determinations

END GROUP	TYPE OF CELLULOSE	D. P.	[η]	D. P./[η]	AUTHOR AND REFERENCE
Hemiacetal	Cellodextrin acetates	8 to 11			Bergmann and Machemer (2)
	"Biosan" acetate	8 to 13			
	Native celluloses	70 to 175			Mark (42, p. 196)
	Regenerated cellulose	75 to 155			
	Cellulose acetate	105			
	"Biosan" acetate	13	0 15	87	Staudinger (55, pp. 463, 491)
	Special triacetates	9 to 35	0 07 to 0 45	97 ±10	
	Native cellulose	50			Freudenberg et al. (18)
	Cellodextrins	30 to 40			
Carboxyl	ClO_2-purified cellulose	96			Schmidt et al. (51)
Tetramethylglucose	"Biosan" acetate	12 to 25			Haworth and Machemer (23)
	Special acetate	100 to 200			

degraded triacetates with molecular weights not exceeding about 10,000 were the results apparently satisfactory. Hess also has found this method to give erratic results (30). On the basis of considerable experience with the method, Mark considers his results, given in table 3, to be of questionable reliability as absolute values (reference 42, p. 196).

Haworth and Machemer (23) have employed the terminal tetrahydroxyglucose residue for molecular weight determinations. Cellulose acetate was converted to a completely methylated cellulose which was then completely hydrolyzed and the yield of tetramethylglucose determined. From this value the molecular weight of the methylcellulose may be calculated to be about 35,000. Unfortunately, the method does not appear to be applicable to cellulose acetates in general, or to other derivatives.

Although, strictly speaking, an end-group determination in the above sense is apparently not involved, Schmidt and coworkers (51) have applied analogous principles to the calculation of molecular weight from their determinations of the acidity (i.e., free carboxyl groups) of various celluloses. Schwarzkopf and Weiss (52), however, deny the suitability of the analytical method, which involved conductometric titration of a heterogeneous system. Regardless of the accuracy of the acidity determination, it is highly improbable that the molecular weights of the different types of celluloses studied by Schmidt et al are really equal, as they infer.

Considering all the end-group determinations, it must be admitted that the results so far obtained are rather meager. The reactions involved are complicated and of limited applicability and the accuracy in the best of cases is not sufficient for the high molecular weights possessed by the technically important materials.

Viscosity method of Staudinger

Although, as pointed out above, it had been generally believed for a good many years that the viscosity of solutions of cellulose derivatives depends upon the molecular weight, no general quantitative relations were formulated until Staudinger discovered that $[\eta]$ for linear polymers of low molecular weight (i.e., having molecular weights within the range of freezing or boiling point methods) is to the first approximation directly proportional to the molecular length and for many cases is relatively independent of the chemical composition. Thus, Staudinger found that $[\eta]$ for solutions of cellodextrin triacetates in *m*-cresol was related to the degree of polymerization, as calculated from molecular weights by the freezing point and Bergmann-Machemer end-group methods, in accordance with the equation[5]

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[5] This is equivalent, within the limits of experimental error, to Staudinger's equation (reference 55, p. 466)

$$\text{Mol. Wt.} = \frac{\eta_r - 1}{CK_m}$$

where $K_m = 11 \times 10^{-4}$ and C is expressed as molarity of glucose residues.

$$\text{D.P.} = 90\,[\eta]$$

The same acetates were carefully saponified with alcoholic potassium hydroxide and the viscosities of the resulting regenerated cellodextrins in cuprammonium were determined. Upon the assumption that no scission of the cellulose chain occurred during regeneration, i.e., that the degree of polymerization of each triacetate and the corresponding cellodextrin was the same, it was found that

$$\text{D.P.} = 100\,[\eta]$$

The regenerated cellodextrins were also nitrated and the viscosities in butyl acetate measured, and again upon the assumption that no degradation occurred, it followed that

$$\text{D.P.} = 77\,[\eta]$$

The methylated derivatives, prepared by the method of Haworth and Machemer, gave somewhat discordant results in that the constant of proportionality varied from 50 to 75, depending on the solvent used (57). Although no actual molecular weight determinations by freezing point or other direct methods were reported for the cellodextrins, nitrates, or methyl derivatives, the approximate constancy of the factor of proportionality (the experimental error being probably ± 10 per cent) is in agreement with Staudinger's viscosity laws and thus confirms the assumption that the chemical conversions did not affect the molecular lengths.

The same close relationship was found between the viscosities of cellulose acetates having $[\eta]$ up to 4 and of the regenerated celluloses and nitrates made therefrom (reference 55, p. 506). Since molecular weights by the Bergmann-Machemer method (over the range where it appeared satisfactory) and the osmotic pressure results of Herzog and Deripasko and of Buchner and Samwel (56) indicated that the direct proportionality between D.P. and $[\eta]$ extended for cellulose acetates to $[\eta]$ = ca. 2.8, Staudinger concluded that the linear relationship extends to the highest values of $[\eta]$ and is applicable to all cellulose derivatives. On this basis, he has estimated the degree of polymerization or molecular weight of many cellulosic materials from viscosity measurements. Thus, he has deduced the degree of polymerization of native cellulose carefully purified in absence of oxygen to be 750 (molecular weight of 120,000), of rayons to be 100 to 200, of so-called high-viscosity nitrocelluloses to be 500 to 2600.

At the present time, it is impossible to predict on theoretical grounds whether there should be a direct proportionality between degree of polymerization and $[\eta]$ of cellulose derivatives or not. The justification for the calculation of molecular weights from viscosity data must rest entirely upon an experimental correlation of viscosity characteristics and molecular weights determined by absolute methods. In so far as cellulose and its derivatives are concerned, the results on this point are promising but not entirely concordant. Although the osmotic pressure results of Herzog and Deripasko and of Buchner and Samwel appear to confirm Staudinger's conclusions, other apparently equally reliable data, summarized in tables 1 to 3, fail to agree. Even in the cases cited, the confirmation may be apparent rather than real, for the measurements of Buchner and Samwel were all made at concentrations too high to give accurate results, and, according to Ubbelohde (59), the viscosity measurements of Herzog and Deripasko are vitiated by a kinetic energy error. A definite parallelism between $[\eta]$ and degree of polymerization is nevertheless evident, and in view of the recognized difficulties in accurately determining high molecular weights, there is reason to suspect that the inconstancy in the values for the viscosity coefficient (D.P./$[\eta]$) obtained by various workers is due to experimental errors.

ULTRACENTRIFUGAL ANALYSIS OF CELLULOSE DERIVATIVES

In order to establish the relationship between viscosity and molecular weight more definitely, we have extended our ultracentrifugal investigations of cellulose to a group of technical cellulose acetates and nitrates. The acetates were acetone-soluble "secondary" acetates having values of $[\eta]$, in acetone solution, ranging from 0.80 to 2.32. Several members of the acetate series were fractionated samples prepared and used by Herzog and Herz (26) in their osmotic pressure investigations.[6] The nitrates contained 12.0 per cent nitrogen and had values of $[\eta]$ ranging from 1.41 to 2.20, corresponding to viscosities of 5 to 71 seconds in 12.2 per cent concentration by the A.S.T.M. standard method (1). For both acetates and nitrates, ultracentrifugal determinations and viscosity measurements were made at 25.0°C. on acetone solutions about 0.1 g. per 100 cc. in concentration. In all cases, the molecular weights found were converted to degrees of polymerization and values of $[\eta]$ were calculated.

Both acetates and nitrates, including the fractionated products, were found to be distinctly non-uniform with respect to molecular weight. The average values, obtained by an approximate method, nevertheless showed a proportional relation to $[\eta]$ corresponding within experimental errors (about ± 10 per cent) to the expressions D.P. $= 230\,[\eta]$ for the acetates and D.P. $= 270\,[\eta]$ for the nitrates. As shown in table 3, our results on celluloses in cuprammonium solvent are given by the expression D.P. $= 260\,[\eta]$. Thus the degrees of polymerization found by means of the ultracentrifuge are from $2\frac{1}{2}$ to $3\frac{1}{2}$ times as great as predicted by Staudinger, his factors of proportionality being respectively 90, 77, and 100.

In interpreting the differences between our results and those of other investigators, it is necessary to consider the effects of non-uniformity. For heterogeneous materials, different methods for determining molecular weights give different "average" values. Thus, it may be shown that freezing point, osmotic pressure, and end-group methods, when applied properly to an ideal mixture, result in an average value defined by the expression

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[6] We are much indebted to Professor Herzog for furnishing us with these samples so that their molecular weights might be determined by two independent methods.

$$M_n = 1 \Big/ \sum \frac{f_i}{M_i}$$

where f_i is the fractional weight of the constituent of molecular weight M_i in the mixture, and the summation is to be applied to all constituents present. This average may be designated as a "number-average molecular weight." On the other hand, the viscosity method, according to Staudinger's theory, should give an average value defined by the expression

$$M_w = \sum f_i M_i$$

which corresponds to a "weight-average molecular weight." The ultracentrifugal method gives a weight-average value. As a consequence, the osmotic pressure method should give a lower apparent molecular weight for a mixture than the viscosity method or the ultracentrifuge method. If the non-uniformity is marked, the difference in the two average values is surprisingly large. In order that the viscosity method for estimating degree of polymerization may give useful results for practical cases where non-uniform products are inevitably involved, it is essential that "weight-average" molecular weights be used in determining the proportionality factor. Staudinger's factors were determined with molecular-weight methods giving "number-averages," and are therefore too small. The improved consistency between viscosity and molecular weight by the freezing point method after fractionation of his samples was taken by Staudinger to mean that the fractionated products were substantially uniform. However, they were probably still distinctly non-uniform (53), and the greater consistency of results really was due to a more nearly constant ratio between the number-average and the weight-average molecular weights following fractionation. Without quantitative information concerning the distribution of molecular weights for a given specimen, it is not possible to convert number-average to weight-average or vice versa, so the magnitude of the error in Staudinger's values due to this factor alone cannot be definitely estimated.

Solvation is another factor affecting molecular weight determinations in various ways. In the case of osmotic pressure measurements in dilute solutions, solvation to the extent of 100 per cent or so has a negligible effect on the calculated molecular weight. The same is true for ultracentrifuge determinations unless the partial specific volumes of the solvated and unsolvated molecules differ, whereupon there is a corresponding error in the calculated molecular weight. For cellulose esters and ethers in organic solvents, the effect is probably not marked. $[\eta]$, on the other hand, is decidedly sensitive to solvation, but the moderate variation in $[\eta]$ with different solvents (10) and the approximate equality of the viscosity coefficients indicate that the solvation of cellulose acetates and nitrates is not large nor greatly different. In fact, if $[\eta]$ is reduced to a volume basis by division by the partial specific volume of the solute (acetate, ~~1.46,~~ 0.66; nitrate, 0.58 ~~1.74~~), as should logically be done when comparing different solutes, the results for cellulose acetates and nitrates in acetone may be expressed by the single equation

$$\text{D. P.} = 156\,[\eta]_{\text{vol.}}$$

Association also may be involved in molecular weight determinations of high polymers, as so often is the case for ordinary small molecules. Osmotic pressure and the ultracentrifuge should give the weight of the associated molecule, other disturbing factors being absent. The effect of association upon the viscosity depends, according to Staudinger's theory, upon the relative positions of the molecules associating together. If compact bundles of parallel molecules are formed, the viscosity is supposed not to be affected, but if two molecules associate end to end, the effect on viscosity is supposed to be twice as great as in the absence of association.

With so many factors influencing molecular weight determinations and viscosities of solutions of celluloses or derivatives, irregularities in the relationship between viscosity and molecular weight probably will persist even with accurate values for molecular weights. Much accurate data for various solvents and at various temperatures must be obtained before the effects of complicating factors can be properly unscrambled. On account of unavoidable non-uniformity, the ultracentrifuge is the only means at present available for obtaining molecular weight information with the necessary detail. Useful information can be secured by osmotic pressure methods, but the experimental technique needs further refinement so that reasonably accurate results can be obtained at low concentrations (e.g., 0.1 per cent or less). In the meantime we believe that the equations we have stated above may be used for estimating the degree of polymerization of technical celluloses, cellulose acetates, and cellulose nitrates by the viscosity method over the range of $[\eta]$ we have studied and with the solvents we have used.

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Page 166. For 1.46 in the 9th line, read 0.66.
For 1.74 in the 10th line, read 0.58.

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THE SORPTION OF BROMINE AND IODINE BY SILICA GEL

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In the literature on the adsorption of gases and vapors by porous adsorbents there is lacking a reasonably complete study on the halogens. There is recorded a set of measurements by Magnus and Müller (3) on the adsorption of chlorine by silica gel in an all-glass system at 0°, 20° and 40°C. They obtained adsorption isotherms which were slightly concave toward the pressure axis. However their results did not fit the Freundlich equation. Some time ago one of us decided to undertake a rather complete study on the sorption of the halogens and the hydrogen halides on various surfaces. This and the following paper give the results for bromine and iodine sorption on silica gel and charcoal.

APPARATUS AND MATERIALS

Measurements of the sorption were made by the static method. The vapor pressure of pure halogen vapor in a glass and quartz system was controlled, and the sorption determined by means of a McBain sorption balance (4).

Figure 1 shows the essential portions of the apparatus. The quartz spring balance was suspended from a hook on a glass ball resting upon three projections in the sorption tube, A. The sorbent was contained in a small glass bucket (1), S, and was suspended from the spring by a quartz fiber. The pressure in the apparatus was determined by the 4.5 turn Bodenstein quartz spiral gauge, B, using this instrument as a null point indicator. The pressure in the jacket of the gauge was varied until the index needle coincided with the fixed reference point viewed in the field of a low-power microscope. The reference point, which was an integral part of the gauge, was attached with wax to the end of a glass tube sealed through the bottom of the jacket in order to prevent damaging vibration. The gauge was mounted in the jacket with a graded seal.

Pressures were read from the large bore, closed-end, mercury manometer with a cathetometer. The manometer readings were corrected to 0°C.

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[1] The material here presented formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Angus E. Cameron in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1932.

Zero readings were taken with the apparatus evacuated or the halogen frozen out with liquid oxygen and the quartz gauge at the temperature at which a run was to be made.

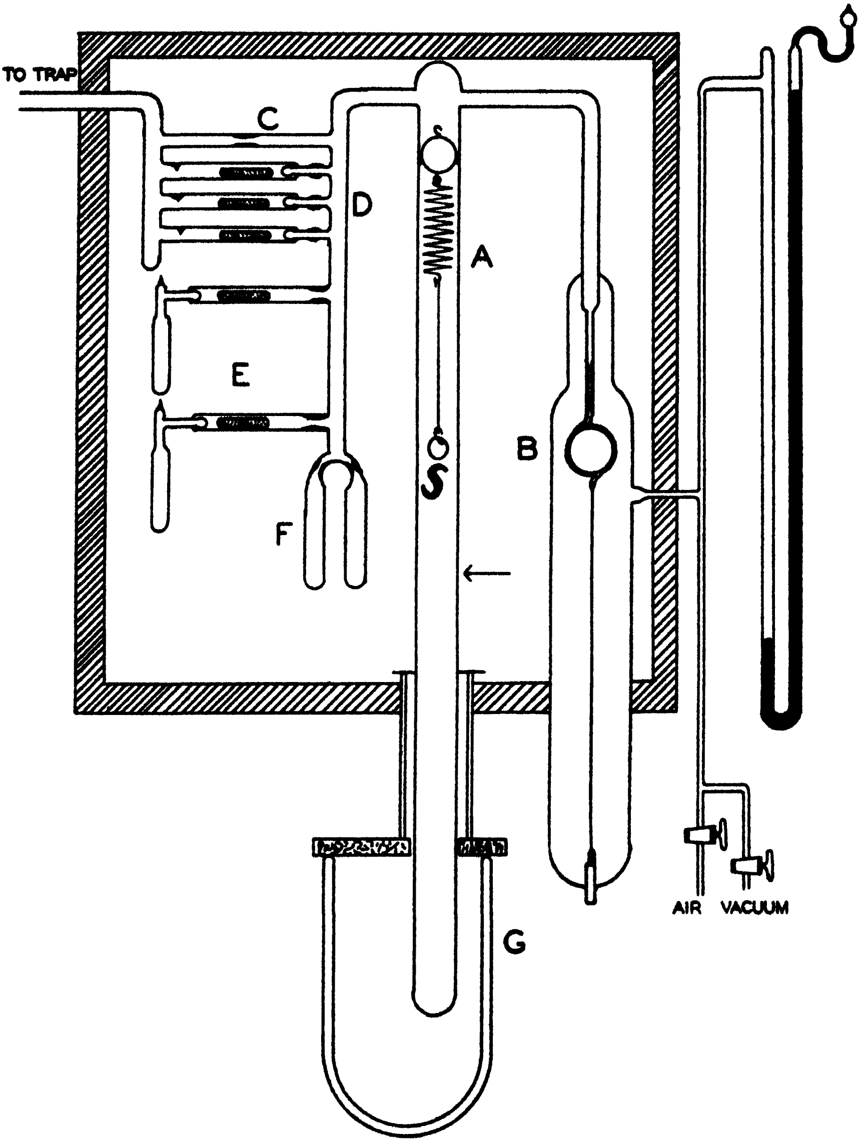

Fig. 1. Sorption Apparatus

The entire apparatus, with the exception of the lower portion of the sorption tube, A, and the bottom of the quartz gauge, was enclosed in an air bath built of wood and lined with asbestos. A multibladed fan at the top of the bath blew air down through a grid of resistance wire. A long, thin-walled glass regulator bulb filled with mercury and connected through a capillary to a control "U" was inserted through the wall of the oven, and operated a thermionic relay device to vary an external resistance in series with the heating grid.

The halogen was introduced into the bottom of tube, A, as will be described, and its temperature was controlled by means of a thermostated bath in a half-gallon Dewar jar. The space between the lid of this small bath and the bottom of the air bath was insulated by a glass tube of large diameter, which was wound with asbestos paper. A resistance wire wound on the inside of this tube permitted heating of this portion of the tube to prevent condensation of halogen when working at high vapor pressures.

The small bath was stirred by a multibladed paddle driven by an induction stirring motor. A special thermoregulator bulb, with large external surface and filled with toluene or mercury, operated a thermionic relay device to control the bath temperature. Above room temperature a small, direct-immersion heating element with a series resistance was used. Water or paraffin oil were used as bath liquid, depending upon the temperature to be obtained. Below room temperature the temperature was controlled by an automatically operated cryostat (2).

The sorption tube was cut at the point indicated by the arrow, and a quartz fiber of sufficient length to extend below the floor of the oven was attached to the one already hanging from the spring. This fiber was shielded from air currents inside the oven by a glass tube of somewhat greater diameter attached to the sorption tube with a ring of cork. A mica pan, weighing about 0.03 g., was hooked to this fiber, and calibrated fractional gram weights were placed upon the pan. The long fiber and pan were weighed on an analytical balance.

Measurements of the spring length were made with a traveling microscope rigidly mounted on a vertical rod supported permanently on the side of the air thermostat. Observations were made through a narrow glass window. Other windows permitted observations of the interior of the thermostat. To reduce thermal disturbances on the inside the latter were double windows. Illumination for reading the spring points was furnished by a long show-case bulb behind an opal glass plate. The opal plate was removed for the studies with iodine vapor and the filament of the bulb lined up behind the spring points.

The traveling microscope was especially designed for vertical mounting and was constructed in the instrument shop of the University of Minnesota. The screw was cut with a 1-mm. pitch and the micrometer head was marked with 100 divisions. The total useful range of the instrument was 100 mm.

The spring was calibrated at the various temperatures both before and after each run. The second calibrations were used in calculations of the sorption. The calibration was carried out in steps of 0.1 g. The sensitivity of the spring, expressed in milligrams per 0.01 mm. elongation, was calculated for each 0.1 g. interval at the different temperatures (see table 1). This sensitivity and the calibration points were used to determine the load on the spring from the observed length.

The weight of the bucket was determined by hanging it on the short fiber and measuring the spring length. About 0.2 g. of sorbent was added to the bucket; after hanging it in place the sorption tube was sealed together. The system was evacuated through tube C. The vacuum system consisted of an ordinary and a high speed Langmuir mercury vapor pump operating in series, with the customary McLeod gauge and liquid air trap.

The portion of the sorption tube in which the sorbent hung was heated with a small resistance tube furnace operated at 500–550°C. During evacuation the connecting tubing was flamed over as much of its length as possible. The system was evacuated at 10^{-6} mm. pressure for 24 hours, and tube C was sealed. The halogen in one of the ampoules, E, was frozen with liquid air, and the breakoffsky operated by a small direct current solenoid which had been placed around the tube before it was sealed in place.

TABLE 1

Spring calibration

LOAD	LENGTH	DIFFERENTIAL SENSITIVITY
grams	*mm.*	*mg per 0.01 mm.*
0.33958	57.051	
		0.17783
0.43944	62.666	
		0.17880
0.53967	67.272	

The halogen was allowed to remain in contact with the sorbent for at least twelve hours. During this time the furnace was held at a sufficiently high temperature to prevent excessive condensation on the sorbent. The temperature was raised to 500°C. several times during the twelve hours to aid in the displacement of foreign gases from the sorbent surface. The ampoule E, containing most of the halogen, was then sealed off, and the system opened to the vacuum line through one of the bank of breakoffskies, D, after the remaining halogen had been frozen out in a seal-off bulb, F, with liquid oxygen.

Evacuation and activation were continued as before for 48 hours, at which time the open breakoffsky was sealed and the second sample of halogen admitted, distilled into the bottom of tube A, and the empty bulb sealed off. The activation furnace was removed when all the halogen had been frozen down in the bottom of tube A, the air bath was brought up to temperature, and the vapor pressure thermostat was assembled and brought into operation. At the completion of a run the halogen was frozen into the remaining bulb, F, and sealed off before opening the system to the vacuum line.

The temperature of the oven was read on a calibrated thermometer suspended beside the sorption tube. The temperature was constant to ±0.15°C., at any setting from 60°C. to 220°C. When working with bromine the temperature of the liquid bath was read on a 100°C. thermometer graduated in 0.1°C. steps and calibrated against thermometers with Bureau of Standards certification. A similarly calibrated 220°C. thermometer reading in 0.2°C. steps was used in the work with iodine. Below 0°C. the temperature of the bath was determined with a calibrated toluene thermometer which for later work was replaced with a ten-junction copper–constantan thermocouple. The temperature of the bath was held to ±0.01°C. above room temperature and to within ±0.03°C. from room temperature to 0°C. Below 0°C. the variation was found to be over a range not greater than 0.08°C.

The same quartz spring was used throughout this work. It consisted of twenty-one turns and was 1.5 cm. in diameter. Its sensitivity was approximately 0.18 mg. per 0.01 mm. elongation. The calibration of the spring was found to be remarkably reproducible, spring lengths measured two months apart checking within a few thousandths of a millimeter under the same load and at the same temperature.

The bromine used was prepared from analytical reagent quality bromine. Further purification was carried out according to the directions given by Scott (6), shaking the bromine twice with 1 *N* potassium hydroxide and once with 0.5 *N*. It was then distilled once from dilute potassium hydroxide solution in an all-glass still with a short fractionating column, and again from the same still after cleaning and drying. The middle portion of the bromine was twice distilled in high vacuum through phosphorus pentoxide which had been resublimed in a current of oxygen. The pentoxide tube was then sealed out of the all-glass apparatus and the bromine thrice fractionated in high vacuum before being distilled into the capsules and sealed off.

The iodine was of C.P. quality and was sublimed once in air from an intimate mixture with C.P. potassium iodide and calcium oxide. The sublimed iodine was then ground with more potassium iodide and calcium oxide, and introduced into the bottom bulb of a series of four bulbs joined by strictured tubing. The column was pumped out and about two-thirds of the iodine driven into the second bulb by heating with boiling water.

TABLE 2

Sorption of bromine by silica gel

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 58.0°C.		
mm.	*millimoles per gram sorbent*	*hours*
0.0	0.0000	3.0
3.7	0.0384	1.5
16.1	0.1238	2.0
38.2	0.2585	1.5
68.6	0.4337	16.0
88.6	0.5514	1.7
113.8	0.7094	3.7
144.7	0.9291	3.0
178.1	1.2134	2.5
239.0	1.8908	10.0
219.1	1.6580*	3.7
198.4	1.4130*	4.7
160.2	1.0650*	3.0
127.2	0.8188*	2.7
99.9	0.6347*	3.5
68.9	0.4433*	6.0
68.7	0.4423*	11.2
58.7	0.3629*	3.0
20.7	0.1705*	2.2
9.0	0.0890*	2.0
5.3	0.0635*	2.0
0.6	0.0230*	1.7
Isothermal at 79.0°C.		
0.0	0.0000	2.0
2.4	0.0105	1.0
11.5	0.0473	1.2
69.8	0.2342	12.7
112.5	0.3601	1.0
162.4	0.5034	1.2
218.6	0.6911	1.7
267.7	1.0144	11.0
326.9	1.0942	2.5
395.4	1.4103	4.0
458.0	1.7697	2.5
520.5	2.1890	1.7
566.6	2.5863	13.0
617.7	3.0396	4.0
671.6	3.6238	4.0
718.7	4.3252	7.0
756.0	4.6483	6.0
Isothermal at 79.0°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
795.1	5.2766	6.0
693.6	4.4618*	5.0
640.2	3.6289*	12.0
547.0	2.4475*	5.5
501.2	2.0126*	5.0
426.8	1.5788*	12.5
365.1	1.2778*	8.2
293.7	0.9758*	2.0
244.2	0.7935*	13.0
174.4	0.5615*	3.5
137.7	0.4511*	3.5
108.5	0.3674*	3.5
64.4	0.2382*	15.0
10.2	0.0516*	3.7
3.9	0.0256*	2.0
0.0	0.0000*	10.0
Isothermal at 99.9°C.		
1.7	0.0036	2.5
12.9	0.0267	0.7
72.6	0.1443	1.2
118.3	0.2210	4.2
151.3	0.2770	1.5
214.2	0.3801	2.0
265.9	0.4665	5.0
324.4	0.5649	3.0
392.6	0.6828	1.0
455.6	0.8028	1.0
336.1	0.5934*	3.0
488.4	0.8752	2.0
564.9	1.0350	3.2
629.6	1.1930	18.0
694.7	1.3616	4.5
744.4	1.4505	3.5
793.0	1.6324	11.0
673.8	1.2929*	26.5
567.0	1.0495*	3.0
473.4	0.8498*	2.0
364.9	0.6466*	6.0
289.2	0.5149*	10.5
235.1	0.4271*	2.0

* Desorption readings.

TABLE 2—*Concluded*

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 99.9°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
173.9	0.3262*	1.7
139.6	0.2698*	1.5
86.6	0.1670*	1.7
68.0	0.1443*	3.0
27.1	0.1081*	2.0
0.0	0.0000*	4.5
Isothermal at 117.5°C.		
0.0	0.0000	11.0
67.7	0.0809	9.5
110.2	0.1262	2.7
139.4	0.1585	2.0
174.2	0.1889	1.5
215.7	0.2295	1.0
266.0	0.2846	3.7
323.5	0.3423	1.5
392.0	0.4076	1.7
470.6	0.4852	2.0
563.1	0.5780	2.0
669.3	0.6888	4.0
790.4	0.8315	1.5
740.0	0.7756*	9.7
614.2	0.6393*	2.5
517.1	0.5330*	2.5
429.8	0.4511*	2.2
356.5	0.3753*	4.0
292.1	0.3118*	8.2
241.2	0.2611*	11.0
194.4	0.2103*	3.2
155.6	0.1806*	1.5
124.0	0.1476*	2.2
74.9	0.1059*	2.5
68.6	0.0838*	10.7
21.1	0.0326*	1.7

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 117.5°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
3.9	0.0109*	2.0
1.2	0.0054*	2.0
0.0	0.0000*	2.0
Isothermal at 137.7°C.		
0.0	0.0000	3.0
68.1	0.0570	11.0
109.6	0.0857	1.5
139.5	0.1039	1.7
173.3	0.1297	5.5
215.7	0.1577	16.2
257.3	0.1907	3.0
323.0	0.2249	3.0
393.8	0.2663	2.7
472.5	0.3186	3.0
563.4	0.3753	3.5
668.6	0.4429	3.0
789.8	0.5214	10.2
751.6	0.4959*	4.0
613.8	0.4102*	2.7
507.3	0.3412*	2.5
432.2	0.2928*	14.5
356.0	0.2456*	3.7
294.5	0.2071*	5.5
239.3	0.1744*	22.0
193.5	0.1446*	2.0
152.8	0.1199*	1.5
122.9	0.0988*	3.0
67.7	0.0559*	11.0
24.3	0.0280*	2.0
9.3	0.0171*	3.0
1.7	0.0080*	2.0
0.0	0.——*	2.5

The bottom bulb was sealed off and the system further evacuated with a mercury pump protected by liquid air trap. Two-thirds of the iodine was then sublimed into the third bulb and the remainder sealed off. The sample tubes, each with a breakoffsky attached, were previously sealed to the top bulb and the iodine driven into them following a third fractional sublimation.

Silica gel used was of the commercial glassy type. It was thoroughly

TABLE 3

Sorption of iodine by silica gel

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isotherm at 98.2°C.		
mm.	*millimoles per gram sorbent*	*hours*
0.03†	0.——	1.7
5.6	0.0143	2.0
10.6	0.0231	10.7
18.0	0.0423	3.0
23.3	0.0787	4.0
13.6	0.0294*	1.7
Isotherm at 137.6°C.		
2.2†	0.01462	3.0
47.4	0.03483	2.0
80.0	0.06375	10.0
120.0	0.2011	9.5
99.6	0.1129*	6.2
15.3	0.0217*	11.5
0.03†	0.0009*	5.0
0.00	0.——	3.5
Isotherm at 158.3°C.		
0.03†	0.——	3.0
15.0	0.0041	1.2
48.2	0.0120	1.5
100.0	0.0269	5.5
144.4	0.0492	9.5
199.6	0.1280	3.5
169.7	0.0743*	1.2
0.03†	0.——*	2.7
Isotherm at 178.4°C.		
0.00†	0.——	14.0
2.6	0.0009	1.5
48.0	0.0071	1.2
101.4	0.0156	2.0
235.1	0.0436	1.5
319.1	0.0905	2.5
428.4	0.3411	9.7
368.4	0.2443*	8.5
169.6	0.0278*	2.2

* Desorption readings.

† Values derived from vapor pressure function.

TABLE 3—*Concluded*

PRESSURE (CORRECTED)	X/M	TIME FOR READING
	Isotherm at 198.5°C.	
mm.	*millimoles per gram sorbent*	*hours*
0.03†	0 —	1.0
46.2	0.0043	1.2
168.7	0 0160	10.0
318.2	0.0333	2.5
423.6	0.0530	1.7
560 0	0.1205	3.5
233.3	0.0236*	1.5
119.5	0 0119*	14.0
0 03†	0.—*	2 0

washed with nitric acid and water and electrodialyzed for two days. The gel was dried and air-activated at 600°C. It was crushed in an agate mortar and sieved, the portion passing 60 mesh and retained by 100 mesh being used in this work. A sample of this gel was ignited to constant weight in a platinum crucible and showed a loss in weight of 3.32 per cent.

RESULTS

Measurements on the sorption of bromine by silica gel were carried out with the adsorbent maintained at 58°, 79°, 99.9°, 117.5°, and 137.7°C., respectively. The vapor pressure of the bromine was regulated by the constant temperature cryostat, G. Equilibrium was established rapidly in the case of silica gel at all but higher pressures. However sufficient time was always taken to insure several constant readings before changing the pressure of the bromine. Data for the measurements are given in table 2. It will be noted that sorption studies were always followed by desorption determinations down to zero pressure. The spring calibrations for the measurements at 58°C. are given in table 1. Similar calibrations were made at the other temperatures, but they are not included in the results. A calculation of the correction for the buoyancy effect of the halogen vapor was made assuming the gas laws and it was found to be less than one-half of 1 per cent of the bromine sorbed at atmospheric pressure. Accordingly no buoyancy corrections were made.

Table 3 gives similar results for iodine. The sorption–desorption isotherms were measured at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C., respectively. Readings were possible up to about 600 mm. pressure. Above this pressure the density of the iodine vapor rendered it impossible to see the spring points even against the bare filament of the lamp. An experimental determination of the buoyancy correction for iodine showed it to be within the limits of experimental error, so no correction was made for this factor.

DISCUSSION

The five isothermals recorded in table 2 are shown graphically in figure 1 of the following paper. Millimoles of bromine sorbed per gram of silica gel are plotted as ordinates against vapor pressure of bromine as abscissae. Similar results are presented in figure 2, also of the following paper, for the sorption isotherms of iodine on silica gel. It is evident from the results that adsorption and desorption are fully reversible. There is no evidence for the hysteresis so often found in sorptions on silica gel. The curves exhibit more or less convexity toward the pressure axis, which indicates loose binding forces and physical adsorption.

Except for slight discontinuities the isotherms for bromine at the higher temperature are almost straight lines. The discontinuities seem to be greater than the probable experimental error and appear to be real. The isotherms for iodine appear to rise more abruptly, but this is in the main due to the change in the ordinate scale. Under comparable conditions many times as many bromine molecules are sorbed per gram of silica gel as iodine molecules. At its boiling point 1.5 millimoles of bromine are adsorbed per gram of gel under a pressure of 200 mm. Under the same pressure at its boiling point only 0.03 millimole of iodine is sorbed per gram of the gel. The International Critical Tables give the critical temperatures for bromine and iodine as 302°C. and 553°C., respectively. It is evident from the data that the amount of sorption here found is not related to the difference between the critical temperature and the temperature at which the sorption was measured, as is the case in so many sorption studies on silica gel.

The data here presented do not fit the exponential equation of the classical adsorption isotherm. Neither do the data fit the Langmuir equation for monomolecular adsorption. The expression which best fits these experimental results is that given by McGavack and Patrick (5). A fuller discussion of the characteristics of the sorption of bromine and iodine by silica gel will be given at a later date. A rather complete study on the sorption of chlorine by porous sorbents is in progress in this laboratory.

SUMMARY

1. An apparatus combining the sorption balance of McBain and Bakr and a quartz spiral manometer is described.

2. Using this apparatus the sorption of bromine by silica gel was measured at 58°, 79°, 99°, 117.5°, and 137.7°C.

3. Using similar technique the sorption of iodine was measured at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C.

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STUDIES ON THE SORPTION OF THE HALOGENS BY SILICA GEL AND CHARCOAL[1]

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There are recorded in the literature several instances of adsorption studies in which one of the halogens was adsorbed by either silica gel or charcoal. Probably the best work to date is that of Magnus and Müller (4), who studied the sorption of chlorine by silica gel in an all-glass system at 0°, 20° and 40°C. Bosshard (2) determined the retention of bromine by various silica gels when the bromine vapor was carried over the gel by an inert gas. Qualitative measurements on sorptions measured dynamically in the presence of foreign gases constitute most of the other recorded measurements. The great difficulties involved in the sorption of halogen vapors have no doubt hindered successful study in this most important field.

Some time ago it was decided to study rather completely the sorption of the halogens in an all-glass–quartz system. Experimental technique in the handling of gases had advanced to such a point that success seemed possible. In this investigation the helical quartz spring sorption balance of McBain and Bakr (5) was combined with the quartz spiral manometer described by Bodenstein and Katayama (1). The design and operation of the apparatus is fully described by the authors in another publication. In brief, the apparatus of all-glass and quartz was sealed from the vacuum pumps during measurements. The vapor pressure of the halogen was maintained by condensing it into a tube immersed in an automatic cryostat as described by Cameron (3). By proper control of the temperature of the bath, the vapor pressure of the halogen could be varied throughout wide limits. The sorption balance and quartz manometer were maintained at constant temperature during measurements in a specially constructed air thermostat. This thermostat was capable of close temperature regulation up to 220°C.

The silica gel used in this investigation was of the glassy type. It was kindly furnished by the Silica Gel Corporation. This gel was digested with nitric acid and then thoroughly washed and finally electrodialyzed for several days in an electrodialysis cell. Following the dialysis it was dried and air-activated at 600°C. Granules which passed a standard 60-mesh and were retained by a 100-mesh screen were used in this investigation. The charcoal was prepared from cocoanut shells which had been cleaned and extracted with ether, alcohol, and water in the order named. The shells were coked by bringing the temperature slowly to 550–575°C. and holding it there for half an hour after the last flammable vapors had been generated. The charcoal was crushed and then activated by passing superheated steam over it in a silica tube heated in an electric tube furnace to 850°C. On analysis this charcoal was found to have an ash content of 0.185 per cent.

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[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

The bromine and iodine were purified chemically by the best recommended procedure. They were then further purified by successive distillations or sublimations in specially constructed vacuum systems. The middle portions only of the final vacuum purifications were used in this investigation.

Sorption–desorption isotherms were obtained over a wide pressure range for bromine on silica gel at 58°, 79°, 99.9°, 117.5°, and 137.7°C. Figure 1 presents the results graphically. Except for the highest desorption readings at 79°C., the sorption and desorption values seem to be completely reversible. Throughout the temperature and pressure range studied there is no hysteresis evident. Slight irregularities may be noted in the curves, and these may be due to errors in the determination. However they seem to be slightly larger than experimental errors and may be evidence for the type of discontinuity reported recently by Allmand and other investigators. The curves obtained for the two highest temperatures indicate that the sorption of bromine is directly proportional to the pressure at these temperatures. The results for the sorption–desorption of iodine at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C. are shown graphically in figure 2. The ordinates of this graph are magnified tenfold as to millimoles adsorbed over figure 1. This makes the curves appear to rise more abruptly in the case of iodine sorption. However the millimoles of bromine sorbed under comparable temperature and pressure conditions were on the average tenfold greater than in the case of iodine. Except at the highest pressures, equilibrium between the silica gel and the halogen vapor was established rather rapidly. There was no evidence for a slow sorption of a different type from the initial rapid sorption. The isotherms for iodine at the two lowest temperatures indicate a slight break in the lowest pressure range. This may indicate a different type of sorption at low pressures.

In the sorption studies on charcoal a very different behavior was found. The rate of sorption was slower than in the case of silica gel, about 24 hours being needed to obtain reasonably constant results. As a result it was decided to determine the rates of sorption and desorption on charcoal. Measurements of this rate were made at constant vapor pressure of the

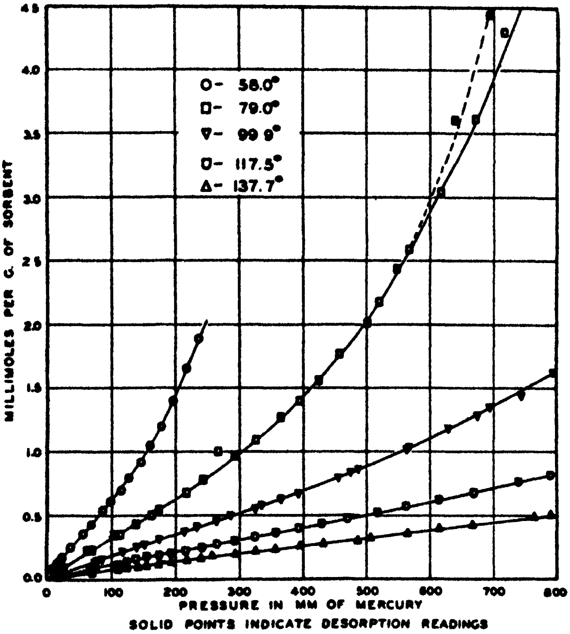

FIG. 1. SORPTION OF BROMINE BY SILICA GEL

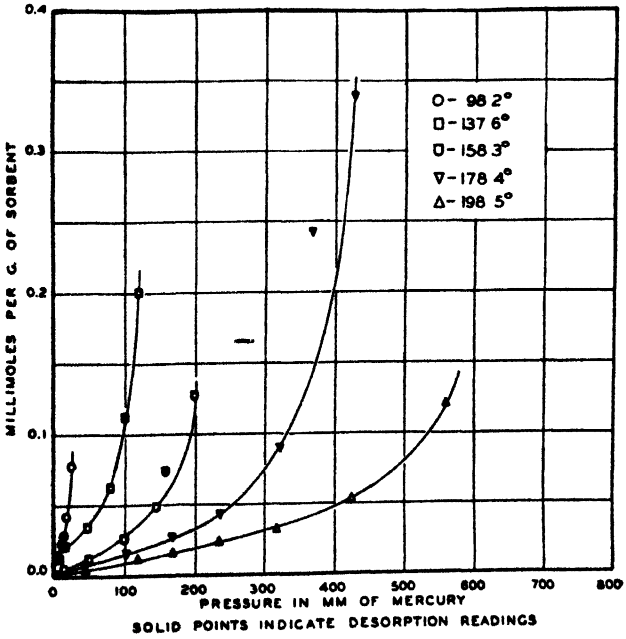

FIG. 2. SORPTION OF IODINE BY SILICA GEL

halogen for 24 hours. The vapor pressure was then increased and the rate of sorption determined for this higher pressure. After sorption at the highest vapor pressure, similar rate studies were made on desorption by successively dropping the vapor pressure of the halogen to the same pressures as were maintained during sorptions. Figure 3 shows graphically the results obtained at 137.6°C. It should be noted that the desorption points reached at the end of the 24-hour period always lie slightly above the corresponding sorption points. It is possible that these points would coincide after a very long time, but the sorption–desorption curves came so close to one another and were so nearly parallel that it was not felt necessary to prolong the study. Rate curves for other temperatures than the one given in figure 3 are much the same. However, the higher the pressure and the higher the temperature the closer to the sorption points lie the desorption points. It should also be noted that more than 2.5 millimoles of bromine remain adsorbed when desorption is carried out at 0.03 mm. pressure. In fact it is impossible to remove all the bromine from the charcoal by thorough evacuation. When the charcoal containing the halogen is heated to about 500°C. and the tube containing the liquid bromine is frozen by immersion in liquid oxygen, equilibrium is reached when slightly more than 2 millimoles of bromine remain sorbed by a gram of charcoal. Under similar heat treatment of the charcoal containing bromine, evacuation of the system was carried out at 10^{-6} mm. pressure. After 24 hours about 0.7

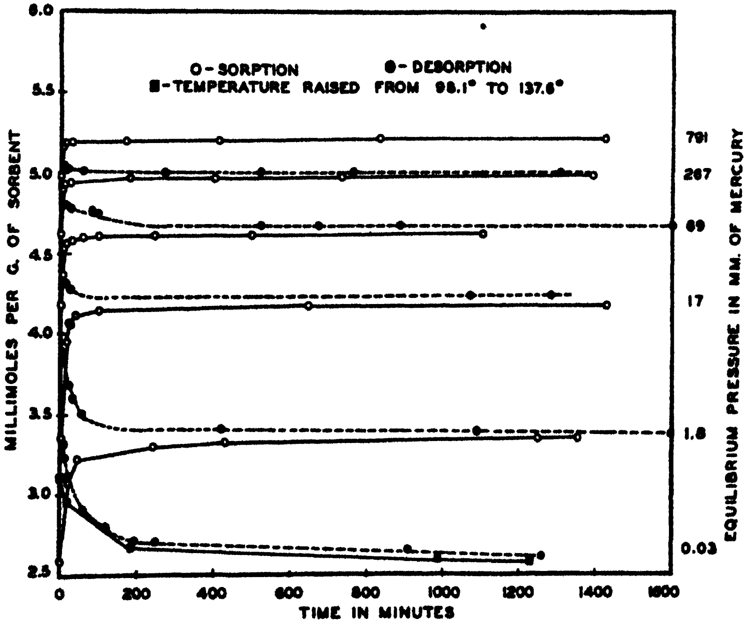

FIG. 3. RATES OF SORPTION OF BROMINE BY CHARCOAL AT 137.6°C.

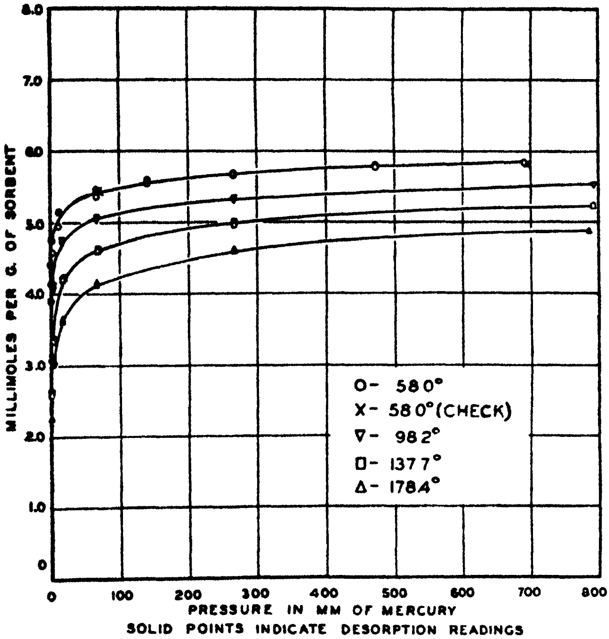

FIG. 4. SORPTION OF BROMINE BY CHARCOAL

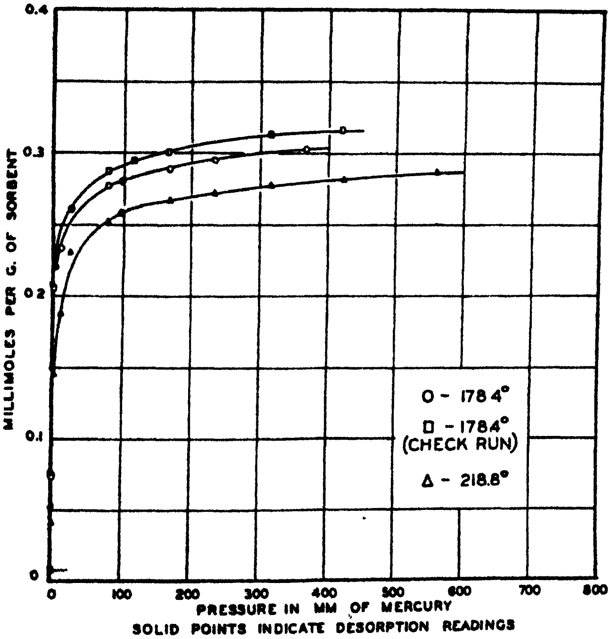

FIG. 5. SORPTION OF IODINE BY CHARCOAL

millimole of bromine remained per gram of charcoal, and at the end of 72 hours this quantity had only been reduced to 0.6 millimole. These results are in agreement with those of Ruff, Rimrott, and Zeumer (6), who found that charcoal must be heated to 1100°C. before the last of the bromine was removed. The products then obtained were hydrogen bromide, bromine, and some carbon-containing bromine compounds.

The isotherms for bromine and iodine sorbed by the charcoal are given in figures 4 and 5. It should be noted that the amount of iodine taken up by the charcoal is much less than the quantity of bromine. However the types of isotherms obtained are similar. The differences in amount of iodine sorbed by the charcoal as compared to bromine are very similar to the differences obtained on silica gel.

DISCUSSION

In considering the character of the sorption of the halogens by two such different porous sorbents, it is important to know the surface area covered by the sorbed gases at various temperatures and pressures. From viscosity measurements Rankine gives the molecular diameters of bromine and iodine as 3.42×10^{-8} cm. and 3.76×10^{-8} cm., respectively. If we assume that the molecules cover an area equal to the square of the diameters, then 1 millimole of bromine would cover 7.1×10^{6} cm.^{2} and 1 millimole of iodine would cover 8.58×10^{6} cm^2. Multiplying the number of millimoles sorbed at varying pressures by these areas would give the approximate area covered under the different conditions. The data obtained for the sorptions by silica gel do not fit the classical sorption isothermal, neither can they be fitted to the Langmuir expressions. The shape of the curves seems to indicate a rather loose type of physical binding of the van der Waals type, or they may represent capillary condensation. In fact the sorption values fit the expression of Patrick,

$$V = K\left(\frac{P\gamma}{P_S}\right)^{\frac{1}{n}}$$

for capillary condensation better than any other, and even here the agreement is not good at either very high or very low pressure values for bromine. The sorption of iodine shows still less agreement with this expression. In order to test this equation it is necessary to know the volume, V, of the liquid sorbed, the surface tension, γ, of the liquid at the temperature of the isothermal, the equilibrium pressure, P, and the saturation pressure, P_S, at the temperature of the isothermal. The data for all the isothermals should fall on the same straight line, where log V is plotted against log $\frac{P\gamma}{P_S}$. The values used in checking the Patrick expression were obtained as follows. The values of P_S were read from a plot of log P against $1/T$.

The values of the vapor pressure used in the graphs and of the surface tension and density at 20°C. of bromine were obtained from the International Critical Tables. The constant of the Ramsay-Eötvös-Shields equation was calculated for bromine and found to be 2.074. Using this constant and the values of the surface tension, γ, obtained by straight line extrapolation between 20°C. and t_c^{-6}, the density of bromine at the temperatures of the various isothermals was calculated. The various values so obtained for bromine are given in table 1.

The values of V and $\frac{P_\gamma}{P_S}$ can then be obtained and the logarithms of these values plotted against each other. Figure 6 shows the results so obtained. The points all lie well along a straight line except at the two extremes, where considerable deviation is to be noted. In view of the many assumptions made use of in obtaining the necessary quantities for the Patrick equation, the agreement seems rather good. In addition, if one reads the equilibrium pressures for the same value of X/M for the various isothermals, then it is possible to calculate the differential heats of sorption from the Clausius-Clapeyron equation.

TABLE 1

$\gamma_{20°} = 41.5$ dynes per centimeter; $d_{20°} = 3.119$; $t_c = 302$°C.

$t_{\text{isothermal}}$	γ	d_t	P_S
			mm.
58.0	36 0	3.14	740
79.0	32.6	3.04	1340
99.9	29.4	3.11	2631
117.5	27.0	3.148	3881
137.7	23.8	3.12	5650

$$Q = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_2}{P_1}$$

The average of eleven such calculations gives the differential heat of sorption as 7719 cal. per mole. The latent heat of vaporization of bromine at the boiling point is given in the International Critical Tables as 7167 cal. per mole. Thus the differential heat of sorption is only slightly larger than the latent heat of vaporization. This difference may be significant, but the sorption forces are apparently not much different from those involved in the formation of the liquid from the vapor phase. Finally the question should be raised as to whether it is necessary to have capillary condensation or not. In these experiments the maximum sorption measured for bromine on silica gel was about 4.5 millimoles at 79°C. $4.5 \times 7.1 \times 10^5$ cm.^{2} gives 31.95×10^5 cm^2. as probably the area covered by bromine. This is not as great as the total surface area per gram of silica gel as reported by many investigators. However, the shape of the isothermals indicates that the gel will continue to take up more of the halogen as its pressure is increased. It is therefore possible that we have capillary condensation superimposed on loosely acting surface forces.

Calculations similar to those given above were made for iodine, but the results did not agree so well with the Patrick expression as did those for bromine. The average of four calculations of the differential heat of sorption gave a value of 11,340 cal. per mole. The latent heat of vaporization at the boiling point is given in the International Critical Tables as 10,516 cal. per mole. However, the heat of sublimation is of the order of 14,520 cal. The differential heat of sorption is thus only slightly greater than the latent heat of vaporization. Similar physical forces seem to be acting in the case of iodine sorption as was found for bromine.

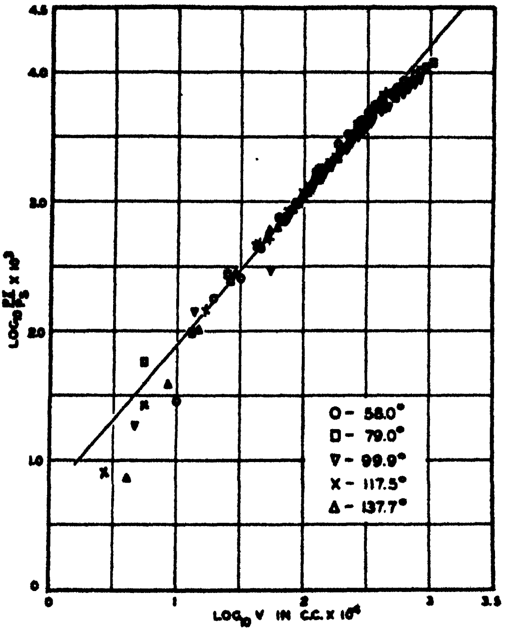

FIG. 6. LOGARITHMIC PLOT OF BROMINE SORPTION BASED ON PATRICK'S EQUATION

As already noted, the character of the sorption of the halogens on charcoal is quite different from that on silica gel. By far the largest part of the sorption occurs in the lowest pressure ranges. There is a relatively small difference between the amounts sorbed at the lowest and highest temperatures at the same vapor pressure of the halogen. This is not true in the case of silica gel. The type of isotherm obtained indicates the formation of a monomolecular layer of sorbed molecules. This appears to be followed at higher pressures by slow diffusion into the charcoal.

The average of eleven values of the differential heat of sorption calculated as before was 11,420 cal. per mole for bromine on charcoal. The average of four such calculated values for iodine was found to be 13,500 cal. per mole. The value for bromine is some 4000 cal. per mole higher than the latent heat of vaporization. In the case of iodine it is about 2500 cal. higher. These significantly higher values indicate that some form of activated sorption is taking place.

The simplest form of the Langmuir sorption expression is

$$\frac{X}{M} = \frac{abp}{1 + bp}$$

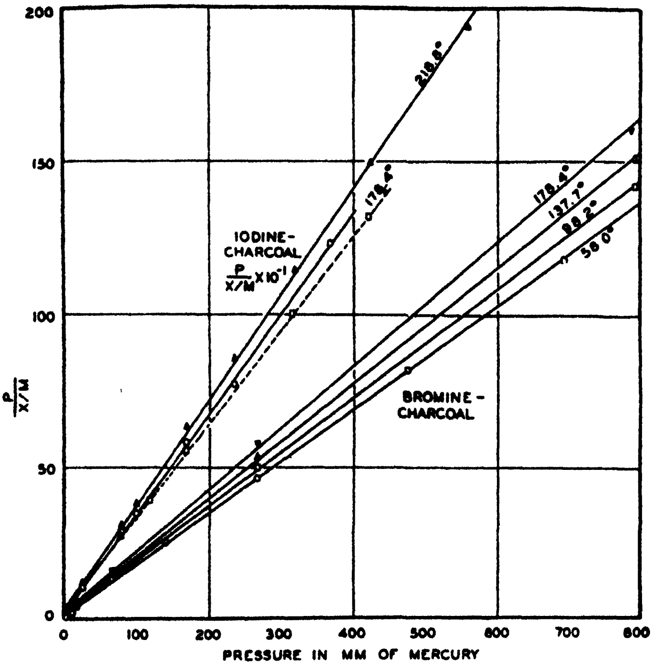

FIG. 7. SORPTION ISOTHERMS OBTAINED BY USE OF THE LANGMUIR EQUATION

which by rearrangement becomes

$$\frac{P}{X/M} = \frac{1}{ab} + \frac{1}{a} P$$

which is the equation of a straight line. The values of $P/X/M$ were calculated from the data and plotted against P. The results are shown in figure 7, and the agreement with the Langmuir equation is excellent. Only when plotted on a much enlarged scale is any deviation from the straight-line relationship found, and this occurs at the very lowest pressure.

It seems evident that the sorption of bromine and iodine by activated charcoal is of the monomolecular type called "persorption" by McBain. In this type of sorption all of the sorbed molecules are bound directly by the atoms of the surface of the sorbent. If the surface of the charcoal is completely covered by bromine molecules, then a simple calculation shows that a gram of this activated charcoal has a surface area of about 350 square meters. This is of the same order of magnitude as found by other investigators.

SUMMARY

1. Sorptions of bromine and iodine on silica gel and activated charcoal have been measured in an all-glass–quartz system at widely different temperatures.
2. Sorptions by silica gel indicate a loose physical binding or capillary condensation.
3. Sorptions by charcoal indicate activated sorption that is monomolecular in depth of layer.

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STUDIES ON OVERVOLTAGE. VIII

OVERVOLTAGE AT BRIGHT PLATINUM ELECTRODES IN 2 NORMAL SULFURIC ACID FOR LOW CURRENT DENSITIES DETERMINED WITH AN OSCILLOGRAPH[1]

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In previous articles the authors have described studies on overvoltage at platinized platinum electrodes in 2 *N* sulfuric acid (a) by means of a commutator in connection with a potentiometer (1, 2, 5, 6), (b) by means of a commutator in connection with an oscillograph (3), and (c) by means of an electromagnetic interrupter in connection with an oscillograph (4). In the present paper the methods described in the last two papers are used to study the overvoltage phenomena at smooth platinum electrodes in 2 *N* sulfuric acid solutions. In all respects except for the type of electrodes, the equipment, general methods of procedure, kind of measurements made, method of recording data, and symbols used are the same as in previous papers and therefore will not be described here.

In the fourth paper (2) of this series the results furnished extremely strong evidence that platinized platinum electrodes in 2 *N* sulfuric acid show no surface resistance of any kind for current densities between 3.8 and 150 ma. With smooth platinum electrodes the decrease in discharge potential was found to be so rapid that satisfactory results could not be obtained with the commutator–potentiometer system. In the fifth paper (3) it was shown that for platinized platinum the commutator–oscillograph method gives results identical with those obtained by the direct potentiometer method; and further confirmation was added to the conclusion previously stated that there is no surface resistance at such electrodes. In the seventh paper (4) an electromagnetic interrupter was used, which made it possible to superimpose various curves in such a manner that a direct comparison could be made between the nature of discharge curves which were known to result only from an *IR* drop and others which were known to result from an *IR* drop and depolarization, and the curve of an unknown type which was under investigation and was known to contain

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[1] The oscillograph used was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

a potential drop due to depolarization and might contain a drop due to surface resistance. It was evident, clearly, from comparisons such as these, that there is no surface resistance at platinized platinum electrodes in 2 *N* sulfuric acid throughout the range of current densities used.

In the works just referred to, the authors have based their conclusions concerning the non-existence of surface resistance upon the assumption that no part of a discharge potential can result from any portion of the charge potential required to force current through a surface resistance. A second assumption has been made, also, that the rate of discharge of potential of an *IR* nature is much more rapid than depolarization. It is entirely upon the latter assumption that many other investigators have based their conclusion concerning the existence of surface resistance, i.e., Newbery (8) and Hollar (7) obtained oscillograms showing vertical drops at the beginning of the discharge intervals which they interpreted as due to a resistance at the electrode–electrolyte interface. The work to be described in the present paper indicates that the early part of the discharge curves at smooth platinum electrodes shows as rapid a drop as that due to a pure resistance. It is shown further, however, that this very rapid drop cannot be due to surface resistance.

Figures 1 and 2 show the behavior of the cathode at different current densities. The potential measured between the two reference electrodes is made up only of *IR* drops between the polarized electrodes and is represented in all figures by *I* when measured by the commutator–potentiometer method and by *I′* when measured by the direct method, i.e., while the polarizing circuit is still closed. The corresponding values for the cathode are represented by *K* and *K′*. The cathode values are the potentials measured between the cathode and cathode standard and might include an *IR* drop due to surface resistance if such exists.

It should be noted that for all current densities the *I* and *I′* values are identical, which means that all potentials due to resistances must be the same irrespective of the method of measurement. At the cathode, for extremely low current densities, the potential is about 1 millivolt less as measured by the commutator method than by the direct; the authors believe, however, that this difference would disappear if a slightly longer charge interval were allowed; it may be observed that the *K* curves were still slowly rising at the end of the charge interval. A similar phenomenon was observed at platinized platinum cathodes. The agreement between the values obtained by the two methods is perfect in all other cases. Probably the most striking difference between these curves for smooth platinum and those reported earlier (3) for platinized platinum is the rapid increase in cathode potential with current density and the rate at which depolarization takes place on the smooth platinum. For instance, according to figure 5 of reference 7 the cathode overvoltage at platinized platinum is less than 2 millivolts for a current density of 0.0084 amp., while from figure 2 of the present article it is about 150 mv. for a current density of only 0.0035 amp.

It is clearly not possible to say from the shapes of the *K* curves of figures 1 and 2 whether the rapid drop represents depolarization only or whether a part is due to an *IR* drop over a surface resistance.

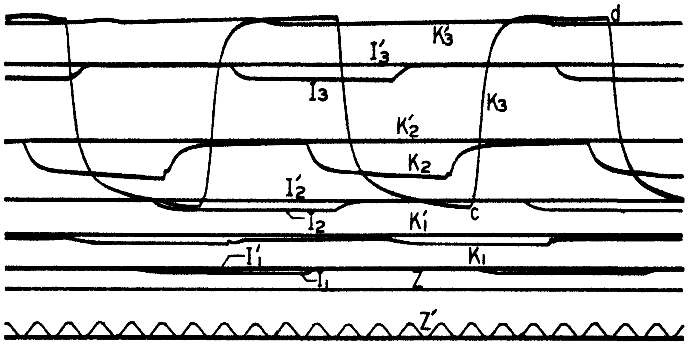

FIG. 1. CATHODE CURVES AND CURVES SHOWING THE *IR* DROP THROUGH THE SOLUTION AT THE CURRENT DENSITIES 0.0004, 0.0010, AND 0.0016 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

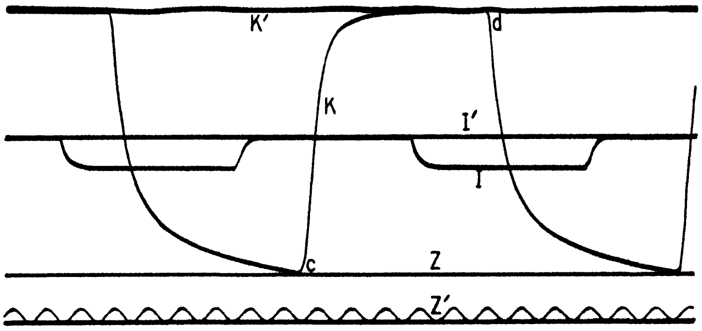

FIG. 2. CATHODE CURVES AND CURVES SHOWING THE *IR* DROP THROUGH THE SOLUTION AT THE CURRENT DENSITY 0.0035 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

The behavior of the anode at different current densities is represented by the curves in figures 3 and 4. The A_3 curves of figure 3 show that at extremely low current densities the anode, also, gives a slightly lower value by the commutator method than by the direct; in fact it shows no drop at all in potential during the discharge intervals. The overvoltage, therefore, under these conditions appears to be zero. The overvoltage at the anode increases extremely rapidly with current density, as the curves in figures 3 and 4 show, but the maximum value attained by the commutator method is precisely the same as that given by the direct method in all cases except the lowest current density. The general nature of the discharge curves is such as would be expected to result from depolarization, though it is not possible to say from the appearance of curve A_3, figure 4, that no portion of the discharge is due to an IR drop. It is evident from these curves that the extent of overvoltage and its general nature is about the same for anode and cathode at smooth platinum electrodes; and the drop in potential is so rapid in both cases that it is not possible to distinguish by means of the commutator between an IR potential and true overvoltage. These observations are distinctly different from those reported for platinized platinum. In order to obtain more information along this line, curves were taken with the electromagnetic interrupter.

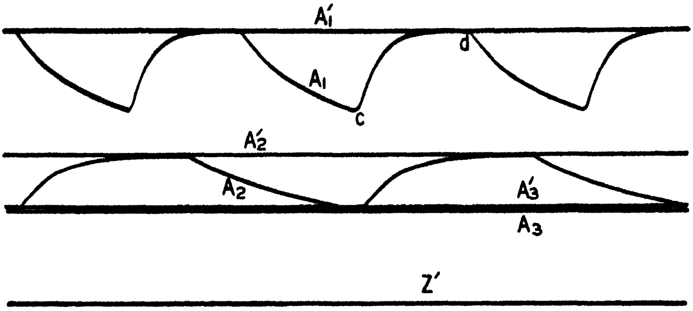

FIG. 3. ANODE CHARGE AND DISCHARGE CURVES AT THE CURRENT DENSITIES 0.000005, 0.00034, AND 0.00071 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

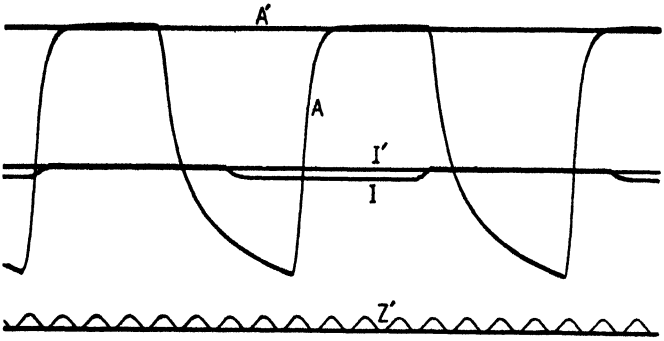

FIG. 4. ANODE CURVES AND CURVES SHOWING THE IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITY 0.0015 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

The action of the electromagnetic interrupter is described in article VII (4) of this series and therefore no description is given here. By means of this arrangement it is possible to superimpose curves representing potentials of different types and different absolute values, and each may be interrupted at the same point on the film. This makes it much easier to analyze the nature of an unknown potential by comparing the curve given by it with curves given by potentials of known characteristics.

In figure 5 the three anode curves, A_1, A_2, and A_3, were obtained at current densities 0.00024, 0.00032, and 0.00163 amp., respectively. The corresponding curves, I_1, I_2, and I_3, show that the potential due to IR drop between the electrodes was practically zero at these low current densities. There are two timing waves at the bottom; the one showing the higher drum speed corresponds to A_3 and the other to A_1. These anode curves appear to represent electrode depolarization only, since there is no vertical portion; but one is liable to be misled unless the speed of the drum is considered. As they appear in the figure, A_3 drops at a greater rate than A_1, yet the film in the case of A_3 had a velocity about 3.5 times greater than in the case of A_1. If the speed of the film had been the same for A_3 as A_1, the rate of drop of A_3 would appear much greater. These curves show: (1) that the anode overvoltage increases very rapidly with current density at low current densities, and (2) that the apparent rate of depolarization increases greatly with the amount of polarization.

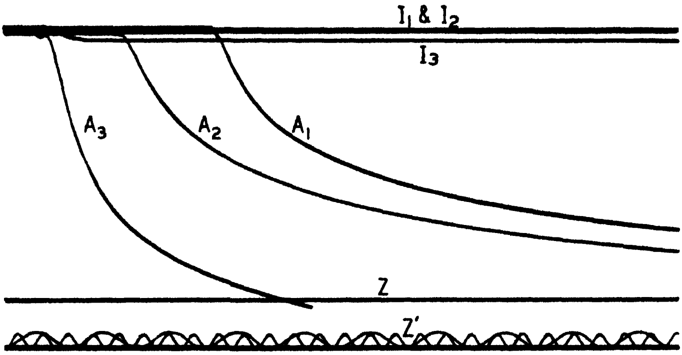

FIG. 5. CURVES FOR ANODE DEPOLARIZATION AND IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITIES 0.00024, 0.00032, AND 0.00163 AMP.

A_1 and A_3 were obtained at different drum speeds

In figure 6 are curves representing overvoltage values determined by three methods. The straight line A' and the straight portion of A_1 were obtained by the constant deflection of the oscillograph mirror due to a continuous constant potential applied to the anode. Both lines correspond to the same potential, but were taken at different times and with different balancing potentials which caused them to appear at different positions on the film. At the end of the straight portion of A_1 the polarizing circuit was interrupted by means of the electromagnet and the remainder of the curve represents the depolarization of the electrode. Curve A was obtained with the commutator for the same polarizing potential as used in the two previous cases. It is evident that the commutator and electromagnet give identical depolarization curves.

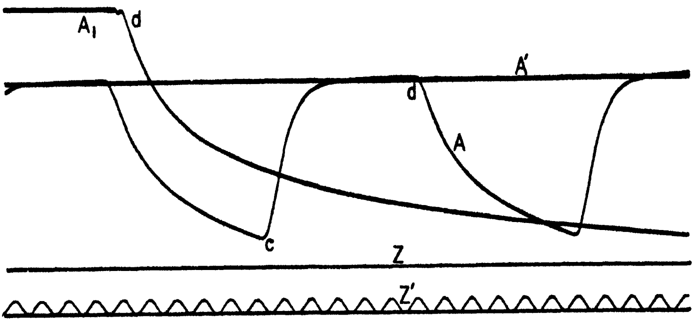

FIG. 6. ANODE CURVES OBTAINED BY THE DIRECT METHOD (A'), THE COMMUTATOR METHOD (A), AND THE ELECTROMAGNETIC INTERRUPTER (A_1)

The same anode potential was used in each case

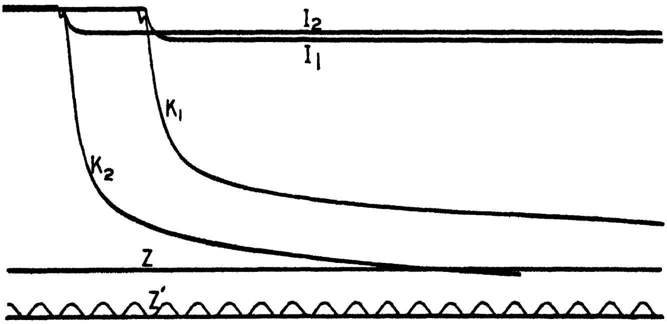

FIG. 7. CURVES FOR CATHODE DISCHARGE AND IR DROP THROUGH THE SOLUTION

The same polarizing potential was used in all cases, but K_2 and I_2 were taken about one half-hour after K_1 and I_1.

The curves in figure 7 were all taken with the same applied polarizing potential across the cell; the only variable factor was time. The K_2 and I_2 curves were taken about one half-hour after K_1 and I_1. During this time interval the overvoltage increased about 40 mv., and the current density dropped from 0.0029 to 0.0028 amp. The drop in the I_1 and I_2 curves is due to the potential across a pure resistance, that of the solution, while the drop in K_1 and K_2 is due to depolarization alone, yet the latter is even more rapid than the former at the start.

Curves for slightly higher current densities are shown in figure 8. The same current density, 0.0067 amp., was used for K_1 and I_1 as for K_1' and I_1', the latter being taken a few minutes after the former. The K_2 and I_2 curves were obtained at a current density of 0.0116 amp. The I curves in this figure represent a sufficiently large potential to show accurately the type of curve given by the interruption of a potential over a pure resistance; this is particularly true of I_2. It is very important to keep in mind that the I_2 curve represents or includes all potentials due to IR drops between the cathode and anode of the electrolysis cell. In other words, if there is any transfer or surface resistance at the cathode it must be included as a part of the drop in I_2. When it is remembered that K_2 is made up only of the sum of I_2 and the true polarization at the cathode, it must be evident that any potential greater than I_2 can be due only to true polarization; or, in other words, all that portion of K_2 below the lower horizontal line of the I_2 curve must be due to cathode depolarization. It is also evident from the curves that there can be no distinction made in the nature of the K_2 curve between the portion above and that below the lower horizontal part of I_2; also, no distinction can be made between the upper part of I_2 and any part of K_2. This all demonstrates that no distinction can be made between a curve representing a fall of potential over a pure resistance and a curve representing pure depolarization for smooth platinum electrodes at the current densities used here. If this conclusion is warranted from the data, then it follows that the oscillograph such as is employed in this work can not be used to disprove the existence of transfer resistance in the case of smooth platinum electrodes merely on the basis of a difference in the shapes

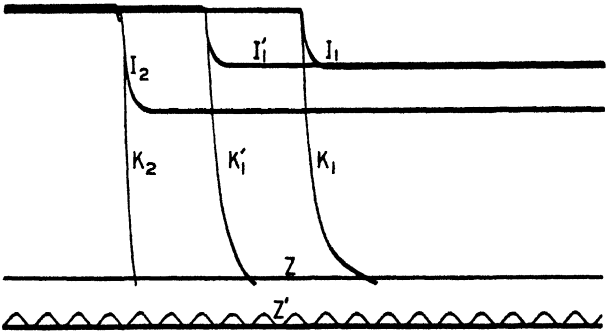

FIG. 8. CURVES FOR CATHODE DISCHARGE AND IR DROP THROUGH THE SOLUTION

K_1' and I_1' were taken at the same current density, 0.0067 amp., as K_1 and I_1, but about five minutes later. K_2 and I_2 were taken at a current density of 0.0116 amp.

of the curves. The authors wish to point out especially, however, that in all of these figures the *I* curves include all *IR* drops, those due to surface resistances as well as electrolytic resistance, and that these drops are small compared with the total drops at the electrodes; also, that current measurements were made in all cases, and when the total resistance was calculated the same value was found irrespective of the total current or whether the electrodes were platinized or smooth.

On the basis of the evidence here presented, therefore, irrespective of the fact that for smooth platinum electrodes it is not possible to distinguish between an *IR* drop and depolarization because both fall so rapidly, yet it may be concluded that there is no transfer resistance even at the surface of smooth platinum electrodes.

SUMMARY

1. A study is made of overvoltage phenomena at both anodes and cathodes of bright platinum in 2 *N* sulfuric acid.

2. An oscillograph was used to obtain charge and discharge curves.

3. Curves are obtained which show the influence of time and current density.

4. A comparison is made of the direct method, the commutator method, and the electromagnetic interrupter.

5. An attempt is made to distinguish between discharge curves due to a pure resistance, those due to true depolarization, and those due to a combination of the two.

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THE APPLICATION OF THE RAYLEIGH INTERFEROMETER TO THE MEASUREMENT OF REACTION VELOCITY

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INTRODUCTION

Duane (6), in 1901, demonstrated that the progress of a reaction in the liquid phase could be determined by measuring the changes in refractive index of the reacting solution. At the same time he showed that the same result could be obtained by measuring the changes in volume of the solution during the course of the reaction. Koelichen (11) had first employed this "dilatometric" method the preceding year. The latter method has since been employed frequently in rate investigations; the former has been almost abandoned. Recently, however, with the increased use of the Rayleigh interferometer, a few investigators (9, 16, 17, 19) have employed that instrument in the determination of rates of reactions. None of these, however, has devoted much space to a description or analysis of his method, which deserves more consideration.

There is a close relationship between the dilatometric and refractometric methods; this is a necessary consequence of the exactness of all the formulas for specific refraction, in which the refractive index is closely inversely proportional to the density. Wagner, Fajans, and Kohner (12), among others, have shown that for completely ionized salts and acids, as well as for unionized substances in aqueous solutions, the molecular refractions calculated from the Lorenz-Lorentz equation and the Biot-Arago law of mixtures are very nearly constants, rarely deviating by as much as 0.5 per cent from their mean values except over very wide ranges of concentration. Since the Lorenz-Lorentz equation is also the soundest, theoretically, of the relations between density and refractive index, we shall employ it in an investigation of the relations between the two aforementioned quantities and the molecular refraction.

For a general reaction

$$A_1 + \dots A_i + \dots A_k \rightarrow B_1 + \dots B_j + \dots B_l \qquad (1)$$

the Lorenz-Lorentz equation before any interval of the reaction is

$$M = p_s M_s + \sum_1^k p_i M_i + \sum_1^l q_j M_j \qquad (2)$$

and after the interval is

$$M' = p_s M_s + \sum_1^k p_i' M_i + \sum_1^l q_j' M_j \tag{3}$$

where the terms $\frac{(n^2-1)}{d(n^2+2)}$ for the various components are designated by M with sub- and super-scripts as indicated below:

M for the solution before the interval of reaction,
M' for the solution after the interval of reaction,
M_i for the reactant A_i,
M_j for the product B_j and
M_s for the solvent.

p_i and q_j are the weight fractions, respectively, of A_i and B_j before the reaction, and p_i' and q_j' their weight fractions after the reaction.

Subtracting equation 3 from equation 2 we obtain

$$M - M' = \sum_1^k (p_i - p_i') M_i + \sum_1^l (q_j - q_j') M_j \tag{4}$$

The weight fractions of the terms remaining on the right-hand side of equation 4 correspond to the quantities consumed and produced according to the stoichiometric equation. That being so,

$$\frac{\text{Mol. wt.}}{p - p'} \quad \text{and} \quad \frac{\text{Mol. wt.}}{q - q'}$$

are the same for all terms.

Multiplying and dividing the right-hand side of equation 4 by this quantity and defining the molecular refraction,

$$R = \frac{\text{Mol. wt.}}{d} \frac{(n^2 - 1)}{(n^2 + 2)}$$

we have

$$M - M' = \frac{p_i - p_i'}{\text{Mol. wt.}_i}\left[\sum_1^k R_i - \sum_1^l R_j\right] \tag{5}$$

The right-hand side of equation 5 we will call K. K is a function only of molecular refractions, which may, in general, be calculated with a fair degree of accuracy, and of concentrations; hence it is readily determinable.

Equation 5 may be solved as a quadratic in $(n' - n)$, the change in refractive index, in terms of the parameters n, d, d', and K. The result is

$$(n' - n) = -n \pm \sqrt{n^2 - \frac{(n^2 + 2)(n^2 - 1)(d' - d) - Kdd'(n^2 + 2)}{d'(n^2 - 1) - d(1 + Kd')(n^2 + 2)}} \tag{6}$$

From equation 6 it is seen that the changes in density, concentration, and molecular refraction must be known in order to calculate the change of refractive index. It is also to be observed that there may be reaction systems wherein there will be a change in density but not in refractive index, and vice versa. Secondly, $(n' - n)$ is very nearly proportional to the change in density, $(d' - d)$, and to K, when these quantities do not exceed the magnitudes encountered in rate work, viz., when $|d' - d| < 0.01$, $|K| < 0.001$.[1] This is illustrated by table 1.

TABLE 1

Change of refractive index as a function of change of density and molar refraction

$(n' - n) = f[K, n, (d' - d), d]$

$K = 0, d = 1, n = 1.333$			$(d' - d) = 0, d = 1, n = 1.333$		
$d' - d$	$n' - n$	$\frac{n' - n}{d' - d}$	K	$(n' - n)$	$\frac{(n' - n)}{K}$
0.1	0 03844	0 3844	+0 01	−0 01773	−1 773
0 01	0 003685	0 3685	+0 001	0 001783	1.783
0 001	0.0003670	0 3670	+0 00001	0 00001784	1.784
0.0001	0 00003669	0 3669	0	0	
0.00001	0 00000366	0 366	−0 00001	+0.00001783	−1.783
0 0	0		−0 001	0 001785	1.785
			−0 01	0 01794	1 794

$d = 1, n = 1.333$

K	$d' - d$	$(n' - n)$	$(n' - n)$ obtained as sum of limiting values from columns 3 and 6 above
−0 01	0 01	0 02184	0.01784 + 0.00367 = 0.02151
−0 00001	0 01	0 003691	0.0000178 + 0.003669 = 0 003687
−0 01	0.00001	0.01786	0.01784 + 0 00000367 = 0 01784
−0 00001	0 00001	0.00002150	0.00001784 + 0.0000367 = 0 00002151

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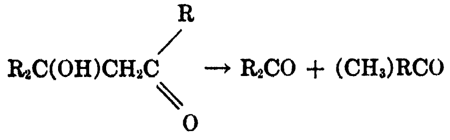
[1] To show that the limiting values for K are reasonable we have calculated the change in molecular refraction for the following reactions:

$$RCN + H_2O \rightarrow RCONH_2 \qquad \Sigma R - \Sigma R' = +0.39$$

$$RCOOR + H_2O \rightarrow RCOOH + ROH \qquad \Sigma R - \Sigma R' = +0\ 17$$



$$R_2C(OH)CH_2C(R){=}O \rightarrow R_2CO + (CH_3)RCO \qquad \Sigma R - \Sigma R' = -0\ 69$$

In dilute aqueous solutions, $(p - q)/\text{mol. wt.} = \Delta N \cdot 10^{-3}$, ΔN being the change in normality, and

$$K = N(\Sigma R - \Sigma R') \cdot 10^{-3}$$

If we take $N = 0.1$, then K falls between 10^{-4} and 10^{-5}.

In dilatometric investigations it has generally been assumed that the small changes occurring in the density are strictly proportional to the changes in concentration. We see from the above considerations that, if the assumption is valid for changes in density, it is also valid for changes in refractive index. However, with the interferometer it is not necessary, although it is convenient and generally satisfactory, to make this assumption, for usually a direct determination may be made of the relation between concentration and refractive index.

EXPERIMENTAL METHOD

The general methods for using the Rayleigh interferometer have been adequately described (1, 2, 4, 7, 10, 20). A very brief description of the instrument will be sufficient here. A beam of light is split into two portions, one of which passes through a length of a "reference" substance, then through a fixed glass compensator plate, the other through an equal length of an "unknown" substance and through an identical compensator plate; finally the beams are reunited through slits to form interference fringes. If the optical paths through the reference and unknown substances are not the same, i.e., if the refractive indices of the solutions are made different, there will result a shift of the fringe system. By adjusting one of the compensator plates by means of a micrometer screw this shift is overcome, and the fringes are brought back to the zero position. Differences of refractive index may be determined as a simple, almost linear, function, of micrometer readings. Two corrections must be applied to the readings to make them a true linear function of the differences in refractive index. These have been treated fully by Adams (1), Barth (2), and others. Crist, Murphy, and Urey (5) have noted recently that in some instruments errors may be introduced, owing to imperfections in the compensator plate mechanism. The substances (liquids or gases) to be compared are placed in the two troughs of a chamber fitted with glass end-plates, and the chamber is then inserted in the instrument so that the two beams of light pass each through one of its troughs.

The instrument used in this investigation was a Zeiss portable liquid interferometer.

Ordinarily it is advisable that the reaction be allowed to proceed in the chamber rather than that the instrument be used for analysis of samples of the reaction solution at suitable times. This is largely a matter of convenience, but uncertainties, which are better avoided, are introduced by the large amount of manipulation required by the latter method.

PREPARATION OF SOLUTIONS

The following discussion is restricted to reactions in the liquid phase. In the simplest case the reaction mixture is obtained by mixing equal amounts of two solutions, A and B, each containing one of the reactants, their concentrations being, of course, double those desired in the experiment. In addition a third solution, C, is prepared of some inert substance such as potassium chloride, which will not react with anything present in solution B. The concentration of C is such that when diluted by half it will give a zero reading in the interferometer when compared to solution A when the latter is diluted by half.[2] Then equal amounts of C and B, previously brought to thermostat temperature, are placed in one chamber; equal amounts of A and B are mixed, the time of mixing being taken as the zero time of the reaction, and are placed in the other chamber. As a consequence of the manner of preparation of the solutions, the readings at zero time should approximate the zero of the instrument. If the kinetic picture is simple, this may be shown to be true by extrapolating the readings to zero time. If, however, there is a rapid preceding reaction, the extrapolation to zero time will give a reading which differs from the zero of the instrument by the change in refractive index of that reaction. Using this method it is possible then to establish with a fairly high degree of certainty[3] the existence or non-existence of preceding reactions. In a similar manner, by using in the reference solution a substance thought to be a product of the reaction, the high probability that it is or is not a product may be established.

Szegö (19), in investigating the oxidation of nitric oxide to nitrogen dioxide, ingeniously took advantage of the fact that there is a change of refractive index in the oxidation, but none in the reaction of nitrogen dioxide to give nitrogen tetroxide. Consequently, with the interferometer he could follow the oxidation without regard for the existence of the following equilibrium. A few other applications will suggest themselves.

After such information on stoichiometry has been obtained, much less care need be taken with the reference solution; it is better, however, to have the readings during a run on the lower part of the scale, so that the corrections will be small and the high differences in dispersion accompanying high differences in refractive index will be minimized.

REDUCTION OF OBSERVATIONS

The problem of the reduction of observations for first-order reactions has been treated satisfactorily by Guggenheim (8). In the method described by him a series of readings $v_1 \ldots v_i \ldots v_n$ are made at times $t_1 \ldots t_i \ldots t_n$ and another series $v_1' \ldots v_i' \ldots v_n'$ at times $t_{1+\tau} \ldots t_{i+\tau} \ldots t_{n+\tau}$. Then from the equation

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[2] The comparison of C and A must be made after dilution because of the shifting of the achromatic fringe, owing to the almost inevitable difference in dispersion of the two solutions. If the differences in dispersion are too large, the fringes will disappear (cf. Hirsch (9)).

[3] This degree of certainty is dependent upon the extent to which reactions are accompanied by changes of refractive index. We have experience only with nitrile, amide, ester, and diacetone alcohol hydrolysis, and with acid ionization (shift of equilibrium in buffers). The change of refractive index is of the same order of magnitude in each of these.

$$kt_i = 2.303 \log_{10} (v_i' - v_i) + \text{constant} \qquad (7)$$

the velocity constant may be obtained. Guggenheim obtained the constant by plotting log $(v' - v)$ against t, but that is entirely incidental to the method. The constant may be obtained by any of four standard methods, viz., by plotting, by a method of averaging, by an unweighted least squares solution, or by a weighted least squares solution. The advantage of Guggenheim's method is that each reading is used once and once only; every point on a graph and every value in a calculation is independent of all other points or values. It is reasonable then to apply sophisticated methods of analysis to the data.

Reed and Theriault (13) have criticized Guggenheim's treatment on the grounds that, since the weights theoretically to be assigned to the points diminish as the reaction progresses, no treatment which neglects this factor can yield better than very approximate results. The statement implies that the graphical reduction of data is essential to the method, and that is not true.

Reed and Theriault (14) conclude a paper on the least squares treatment of first-order reactions with the rather extreme statement that, ". . . . the least squares treatment should be used whenever the velocity constant is to be determined within an allowable error of, say 5 per cent."

It is a fact not very generally recognized that whenever a very considerable body of data is at hand, almost any reasonable method of reducing that data to a final result will yield a result very close to the best value obtainable from a theoretically perfect least squares solution. A preliminary demonstration of the truth of this statement may be given by calculating velocity constants from the sample data given by Guggenheim. There are two sets of data taken during a single run, with twenty pairs of points in each. The constants are calculated by the four formulas given below, and the constants obtained are given in the right-hand columns:

$k\ (\times\ 0.4342 \times 10^3)$

(1) Graphically (by Guggenheim): 6.54 6.56

$$0.4342kt_i + \log (v_i' - v_i) = \text{Const.} \qquad (8)$$

(2) Method of averages 6.558 6.566

$$0.4342k = -\frac{\sum_{1}^{n/2} \log (v_i' - v_i) - \sum_{n/2+1}^{n} \log (v_i' - v_i)}{\sum_{1}^{n/2} t_i - \sum_{n/2+1}^{n} t_i} \qquad (9)$$

(3) Unweighted least squares: 6.565 6.568

$$0.4342k = -\frac{n\sum_1^n t_i \log(v_i' - v_i) - \sum_1^n t_i \sum_1^n \log(v_i' - v_i)}{n\sum_1^n t_i^2 - \left(\sum_1^n t_i\right)^2} \qquad (10)$$

(4) Weighted least squares: 6.556 6.565

$$0.4342k = -\frac{\left[\sum_1^n (v_i' - v_i)^2\right]\left[\sum_1^n t_i (v_i' - v_i)^2 \log(v_i' - v_i)\right] - \left[\sum_1^n t_i (v_i' - v_i)^2\right]\left[\sum_1^n (v_i' - v_i)^2 \cdot \log(v_i' - v_i)\right]}{\sum_1^n (v_i' - v_i)^2 \sum_1^n (v_i' - v_i)^2 \cdot t_i^2 - \left[\sum_1^n (v_i' - v_i)^2 \cdot t_i\right]^2} \qquad (11)$$

It is fairly obvious that the graphical method is not sensitive enough to do full justice to the data, but the uncertainty introduced by using any of the first three methods as alternatives for the weighted least squares is of an order of magnitude far less than 5 per cent.

While with accurate data it is thus apparent that the uncertainty introduced by using a less exact method of calculation may be reduced to a small quantity, there is yet no indication of the relationship between that uncertainty and the probable error which arises from accidental errors in the data. To shed light on this point four identical runs were made at low concentrations (0.005 N) to insure large probable errors in the results, which are given in table 2. The data are admittedly not sufficiently ample to be entirely convincing, but the indications are clear. The weighted least squares result is to be taken as the standard with which the other three are to be compared. The graphical method appears to be the least reliable, since it gives the largest deviations from the weighted least squares solutions. The solutions by averages and the unweighted least squares solutions give results which are of about the same reliability; since the latter method is somewhat more laborious, we shall discard it in favor of the method of averages. The differences between the constants obtained by averaging and those obtained by weighted least squares are all less than the probable error in the latter constants, averaging about two-thirds of the probable error.

The principle that the uncertainties introduced by calculations must be negligibly small in comparison with the experimental error, is indisputably sound in the common situation where the calculations form the lesser part of the investigation. There is, on the other hand, practical justification for using a less precise method of calculation in those situations where the time required for a least squares solution would be a major fraction of the total time required for the work. In rate investigations there is a place for each of the methods with the exception of the third. The graphical method is the best when there are trends toward the end of the experiment due to complications such as often appear in organic reactions. These are usually of such an involved nature, or are so incompletely understood, that they may not be treated exactly, but the observer is, none the less, perfectly justified in giving less weight to points obtained after the appearance of the trend. On the other hand, if there are no systematic trends, if a fairly large amount of data can be obtained in each run, and if there are a large number of runs to be handled, then the method of averages is the most satisfactory solution. If the quantity of data is comparatively small and is characterized by a relatively high probable error, then the fourth method will give best results. Furthermore, if the data are known to be characterized by certain simple constant errors of known type, then the method described by Reed and Theriault finds its application.

TABLE 2

Rate constants for runs calculated by four methods

RUN NO	RATE CONSTANTS			
	1 Graphical	2 Averages	3 Unweighted least squares	4 Weighted least squares
1	0.03823 ±0.00057	0.03809 ±0.00059	0.03805 ±0.00066	0.03853 ±0.00056
2	0.03959	0.03973	0.04007	0.03982
3	0.04003	0.03924	0.03853	0.03878
4	0.03894	0.03779	0.03735	0.03802
Mean	0.03927	0.03868	0.03841	0.03885

Probable errors determined for each method by the external consistency of the four constants.

In the interests of greater accuracy two cautions are to be observed. The time between the two readings of each pair should be equal to two or three half-times of the reaction. Roseveare (15) has shown that the rate constant is most accurately determined from two points, if the second occurs at two-thirds completion of the reaction. Accordingly, it is well to plan a concentration of points at the beginning of the reaction and another concentration near two-thirds completion.

Higher order reactions must still be treated by the methods developed for ordinary chemical analysis, which are apt to be, with this instrument and the dilatometer, incapable of yielding very reliable results. Roseveare has given an equation which eliminates the necessity of obtaining the infinite time reading directly for the bimolecular reaction, where $dx/dt = k(a - x)^2$.

RELIABILITY OF THE INTERFEROMETER

Returning to an examination of the data given in table 2, and adding the data from which the constants in run No. 1 (see table 3) were obtained, we find evidence that the systematic errors introduced by the interferometer are very small.

If a number of readings be made with the interferometer chambers empty, the probable error of a single reading, determined from the degree of consistency of the readings, is on our instrument about 0.2 division. In run No. 1 the probable error in ($v' - v$) is 0.18 division as determined by the internal consistency of all the readings, that is, by the formula

TABLE 3

Results obtained in run No. 1

$k = 0.03809$

t	v	t'	v'	$v' - v$	$v' - v$ (calcd.)	RESIDUALS
minutes						
3	106.8	63	133.2	26.4	26.0	0.4
4	108.3	64	133.4	25.1	25.0	0.1
5	109.3	65	133.7	24.4	24.2	0.2
6	110.5	66	133.9	23.4	23.2	0.2
7	111.7	67	134.0	22.3	22.4	0.1
8	112.9	68	134.3	21.4	21.5	0.1
9	114.0	69	134.3	20.3	20.7	0.4
10	114.5	70	134.6	20.1	19.9	0.2
11	115.6	71	134.5	18.9	19.2	0.3
12	116.1	72	134.6	18.5	18.4	0.1
13	117.1	73	135.0	17.9	17.8	0.1
14	117.8	74	134.9	17.1	17.1	0
15	118.6	75	135.0	16.4	16.5	0.1
16	119.6	76	135.0	15.4	15.9	0.5
17	120.0	77	135.2	15.2	15.2	0
18	120.8	78	135.2	14.4	14.7	0.3
19	121.0	79	135.2	14.2	14.1	0.1
20	121.2	80	135.1	13.9	13.6	0.3
21	122.0	81	135.4	13.4	13.1	0.3
22	122.5	82	135.3	12.8	12.6	0.2

$$r = 0.6745\sqrt{\frac{\sum w_i^2}{n-2}} \qquad (12)$$

where w_i is the residual $(v_i' - v_i)_{\text{obsd.}} - (v_i' - v_i)_{\text{calcd.}}$ The readings v_i' were each taken three times; assigning them a proper weight, the law of propagation of errors gives the probable error in v_i equal to 0.16. The agreement between this value and the one obtained from direct readings indicates that the first-order rate equation is satisfactory. The probable error in the velocity constant, arising from this probable error in v, is found to be 0.00046. The probable error in the constant obtained from the external consistency of the four runs is 0.00059. Birge (3), in his treatment of the problem of internal and external consistencies, has shown for the case where there are four functions being compared, that owing to statistical fluctuations, the ratio of probable error from external consistency to that from internal consistency should be 1.24. It is in the case given above, fortuitously, 1.28. A much less close agreement would still be a strong indication that there are no systematic errors, which vary only from run to run.[4]

TEMPERATURE CONTROL

The commercial instrument is very inconveniently thermostated. Fairly satisfactory results were obtained within five or ten degrees of room temperature by pumping distilled water through 30 ft. of copper tubing in a thermostat, and then through the reservoir which surrounds the chamber containing the solutions. By making heavy brass cover plates for the chamber, of the type described by Cohen and Bruins, but hollow so that water could be drawn through them, the temperature regulation was made very satisfactory within ten degrees of room temperature and reasonably so within fifteen. The difficulties arising are due not to temperature variations which affect the rates of the reactions, but rather to much smaller inhomogeneities of temperatures, both in the reacting solution and in the surrounding bath, which affect the refractive indices enough to make the fringes very unsteady. A thermostat controlling the temperature to 0.01°C. should be satisfactory provided there are no sudden changes of temperature within it amounting to more than 0.002°C. It is not possible with the present design of the instrument to obtain temperature coefficients over a wide range of temperature.

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[4] Since the above was written it has been found that the instrumental defect described by Crist, Murphy, and Urey (5) is more common than might have been suspected. Results as consistent as those given above cannot be obtained from an instrument having an appreciable error of the type described. This error appears when the tip of the micrometer screw is not in the axis of the screw. A deviation of 0.05 mm. is sufficient to produce the results described by Crist, Murphy, and Urey. The error is periodic, going through a cycle in one complete turn of the micrometer screw. It disappears when the lever arm on which the screw acts is perpendicular to the screw. It was under these special conditions that the runs described above were made.

Crist, Murphy, and Urey calibrated their instrument by measuring each fringe throughout the whole scale. Adopting different tactics, we removed the micrometer screw from our instrument and reground the tip so as to center it. This can be done only on a very good lathe. After this treatment no regular periodicity could be found.

If this correction is not made, systematic errors as large as 2 per cent may appear in the rate constants when the concentrations are as low as those described above. At higher concentrations the errors become much less important.

If the heat of the reaction is large, the temperature of the reacting solution may rise slightly above that of the thermostat and the reference solution; this results in a very easily perceptible change of refractive index. From the nature of the relations involved it appears that the temperature difference reaches a maximum in a very few minutes, but is dissipated slowly, and exists as a potential source of error throughout three-quarters of the life of the reaction. For first-order reactions this potentiality disappears when we examine the situation more closely.

The temperature difference is given by the equation

$$(T - T_0) = \frac{\Delta H A_0 k}{1000(K - k)} \left[e^{-kt} - e^{-Kt} \right] \tag{13}$$

which is the solution of the differential equation,

$$\frac{dT}{dt} = -K(T - T_0) - \frac{\Delta H}{1000} \frac{dA}{dt} \tag{14}$$

k is the velocity constant, K the Newton's law of cooling constant, ΔH the heat of reaction in calories per mole, and A_0 the initial concentration of the reactant. We may set the observed reading at any time equal to the correct reading at that time plus the difference due to the temperature difference, so that

$$v_i = V_i + x_i \tag{15}$$

x_i is directly proportional to the change in refractive index due to the temperature disturbance and so is directly proportional to the temperature difference. Therefore we may say in any given case that

$$x_i = C_1 \left(e^{-kt} - e^{-Kt_i}\right) \tag{16}$$

Now the exponential form of the first-order rate equation is

$$(V_i - V_\infty) = (V_0 - V_\infty)\, e^{-kt_i} \tag{17}$$

Eliminating x_i and v_i from equations 15, 16, and 17, we have, x being zero at both zero and infinite time,

$$(v_i - v_\infty) = (v_0 - v_\infty - C_1)\, e^{-kt_i} + C_1\, e^{-Kt_i} \tag{18}$$

As soon as the second exponential term becomes negligible with respect to the first, the temperature difference will have no influence on the rate constant. In a plot of log $(v_i - v_\infty)$ against time the observed result would be that the y-intercept would be log $(v_0 - v_\infty - C_1)$ rather than log

($v_0 - v_\infty$), while the slope would be unchanged. In a particular case at hand ΔH was about 18,000 cal., k was 0.0201 min.$^{-1}$, K for the interferometer chamber (all the metal chambers should give about the same value) was roughly 0.85 min.$^{-1}$, and A_0 was 0.05 N. The maximum temperature difference should be 0.019°C., occurring at 4.51 minutes. At that time the second exponential term is nearly negligible, and by eight minutes it is completely so. The temperature difference does not fall to the point where its effect on the refractive index is negligible for over two hours. In two runs where the first point was at fifteen minutes, there were no trends; in a third where the first point was at three minutes, there was a very definite trend, and the rate constant was two or three per cent lower.

For higher order reactions the same situation may be found; the matter has not been investigated, and there is no certainty that such is the case.

After several of the chambers had been used for some time, baffling irregularities began to appear in the results. It was finally found that the cement holding the end-plates in place had been partially dissolved away and the chambers had developed small leaks which resulted in a slow change of the refractive index of the solution. This is undoubtedly the source of the drift which was attributed by Stewart and Kung (18), in their use of the method, to unequal evaporation from the two chambers.

A COMPARISON OF THE MERITS OF THE DILATOMETER AND THE INTERFEROMETER

In its present design the interferometer is less flexible than the dilatometer; it can not be used over a wide range of temperatures; certain waxed joints must be protected if non-aqueous solvents are to be used; it is probably not applicable to reactions which are highly photosensitive throughout the range of visible light. Moreover the instrument is expensive. On the other hand the interferometer will normally handle faster reactions; it requires less care in thermostating; and when calibrated interferometers are available (in use for ordinary analytical work) results may be obtained with a minimum of effort. If only small amounts of reagents or solvents are available, experiments may be made in favorable cases with as little as 0.05 cc. of solution. It is difficult to compare the sensitivities of the two methods, since the practical consideration of temperature control constitutes the main restriction to the extension of the sensitivity of the dilatometer. Finally, as noted above, with the interferometer the presence or absence of rapid preceding reactions or of equilibria may be demonstrated with high probability.

SUMMARY

1. The quantitative relations between change of density and change of refractive index during reactions have been derived. It has been shown

that the change of refractive index is as reliable a measure of the progress of a reaction as is the change in density.

2. Practical methods for the application of the Rayleigh interferometer to rate measurements have been described.

3. It has been shown that the interferometer can be of value in the investigation of the stoichiometry of a reaction.

4. The reduction of observations has been discussed in some detail. Guggenheim's method is recommended for first-order reactions, and the method of averages is found to be the most convenient and, in general, a sound and thoroughly reasonable means of obtaining velocity constants.

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THE THIXOTROPY OF HEATHER HONEY

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The use of the viscometer for testing the purity of honey was introduced in 1911 by Fellenberg (4), who tested honeys mixed with water in an Ostwald viscometer. Eisenschitz (3) has shown that honey mixed with water behaves as a normal viscous liquid. It is known, however, that some undiluted honeys, even when not granulated, show abnormal viscous behavior (6), and de Boer and Kniphorst (1) have shown that stirred heather honey (from *Calluna vulgaris*) increases its viscosity gradually on standing. The rate at which this rise in viscosity takes place depends on the temperature, passing through a minimum at about 15°C., but even at this temperature, the viscosity (as measured by the time of outflow per gram from a Holde viscometer)[1] increases by many fold within twenty-four hours. On stirring, the viscosity returns to somewhere near its original value. This phenomenon is described by de Boer and Kniphorst as "thixotropy," but since it is not known how far this is really similar to the reversible sol-gel transformations to which the term thixotropy was originally applied, it is of interest to investigate further the viscous and rigid properties of the sol and gel forms. No information seems to be available, for example, as to whether the stirred honey is a true fluid, which on standing sets into a rigid gel; whether the setting is caused by a rise in viscosity only; or whether both sol and gel forms show rigid properties. Moreover, the phenomenon has a practical interest, since heather honey, by reason of its gelatinous character, holds its water in a different way from other honeys. Ordinary honey containing more than about 20 per cent of water (due to either immaturity or dilution) tends to ferment, whereas heather honey, since some of its water is held in an immobilized condition, does not do so until a considerably higher moisture content is reached. The term "heather honey" is used to describe any honey derived largely from the nectar of *Calluna vulgaris*, *Erica cinerea*,[2] and allied species. However, in many cases heather honeys are not obtained from a pure heather source, samples showing a range of properties between those of a honey obtained entirely from heather on the one hand, and of an ordinary non-thixotropic honey on the other. A method of assessing the extent to which a given sample showed the gelatinous and thixotropic properties of a heather honey would be of value in deciding whether an apparently excessive moisture content would be likely to lead to subsequent spoiling due to fermentation.

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[1] For a description of this instrument see Lunge-Berl Chemische Technologische Untersuchungen, 7th edition, Vol. III, p. 461.

[2] Added January, 1935: It now appears probable that honeys derived from *Erica* alone are not thixotropic.

THE GEL FORM

To investigate the properties of the gel form, a ball viscometer was used. As a preliminary experiment, in view of the fact that only comparatively small samples were available, and that viscometer vessels could not, therefore, be very large compared with the size of the balls, the effect of wall-correction on the viscosity measurements on a normal liquid (Lyle's Golden Syrup) was tested.

TABLE 1

Rate of fall of balls through Lyle's Golden Syrup

DIAMETER OF BALL	TIME	$\frac{\text{VELOCITY}}{\text{DIAMETER}^2}$
inches	*seconds*	*arbitrary units*
1/2	34.5	0.116
5/16	52.3	0.194
1/4	65.0	0.247
7/32	81.5	0.256
3/16	98.5	0.291
5/32	126.2	0.329
1/8	175.0	0 356

A Nessler tube of internal diameter 3.1 cm., having marks etched at a distance of 6 cm. apart, was filled with syrup, and left to stand overnight. On the following morning, a number of steel balls were dropped through the liquid, the time in seconds taken to fall between the marks being recorded.

The balls are not small compared with the size of the tube, and the results given in table 1 show that the rate of fall is by no means proportional to the square of the diameter of the ball.

Although various corrections have been proposed to allow for such errors (5), it seemed more satisfactory to eliminate differences in the error by using two balls of different size, falling in vessels whose diameters bear an approximately constant ratio to the diameters of the balls.[3]

For this purpose, two glass cylinders were chosen, A having a diameter of 3.4 cm., and B a diameter of 4.8 cm. Into A were dropped balls of diameter 0.80 cm. ($\frac{5}{16}$ in.), and into B balls of diameter 1.11 cm. ($\frac{7}{16}$ in.). For a true fluid, in which the viscosity is independent of shearing stress, the times taken for the balls to fall between the marks (5 cm. apart in each case) should bear a ratio equal to the ratio of the squares of their diameters.[4] Moreover, for a true fluid, the rate of the fall should be unaffected by stirring.

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[3] I am indebted to Dr. R. K. Schofield for suggesting this arrangement.

As a first experiment, balls were timed to fall through a sample of Lyle's Golden Syrup (a different sample from that used in the earlier experiment). Immediately after the test, a perforated metal disk was forced twice up and down through the syrup so as to cause a thorough stirring, and the test was repeated.

The test was repeated exactly with a sample of heather honey which had been left in the viscometer vessels overnight. It is clear from table 2 that whereas syrup has a viscosity which is reasonably independent of both stress and stirring, heather honey shows a variable viscosity in its unstirred state, and that its viscosity falls enormously after stirring.

TABLE 2

Viscosity of Lyle's Golden Syrup and heather honey

FLUID	VELOCITY IN CM. PER SECOND		VELOCITY/D^2	
	A	B	A	B
Lyle's Golden Syrup				
Before stirring	0.108	0.217	0.171	0.176
After stirring	0.110	0.216	0.175	0.176
Heather honey				
Before stirring	0.0475	0.137	0.076	0.112
After stirring	0.395	0.770	0.625	0.625

Two heather honeys were used in these experiments, designated X and Y. The experiments were performed at room temperature, 15°C.

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[4] As a first approximation, to account for the effect of the walls of the containing tube (which is assumed to be infinitely long) Ladenburg (Ann. Physik **22**, 287 (1907)) has proposed the introduction of a term into the denominator of the Stokes equation, which then reads:

$$\eta = \frac{2r^2(\rho - \rho')g}{9v(1 + Ar/R)}$$

where r is the radius of the sphere
R is the radius of the tube
ρ is the density of the sphere
ρ' is the density of the medium
v is the velocity of the fall
η is the viscosity, and
A is a pure number.

Since the correction term $(1 + Ar/R)$ does not involve viscosity, the times of

To find whether this "gel" shows any marked yield value (i.e., whether the viscosity becomes practically infinite for very small stresses (cf. Scott Blair (9)), a very small ball (diameter ⅛ in.) was placed just below the surface of a sample of heather honey (Y). After some hours, it was clear that the ball had fallen appreciably; thus, although the viscosity is very high for such small stresses, it is unlikely that there is any sharp yield value for the gel.

THE SOL FORM

To find out whether the thoroughly stirred honey (the sol) behaves as a true fluid,[5] a sample of Y was stirred in the manner described above, and tested in the Rothamsted plastometer. This instrument has already been described (2, 8), and it will suffice to say that in it the material is forced by compressed air through a capillary tube of known dimensions under varying pressures, the amount of flow per second being recorded for each pressure. The plastometer thermostat was set first at 15°C., and, for a second experiment at 30°C. At the latter temperature, two different capillary tubes having radii of 0.088 cm. (No. II) and 0.048 cm. (No. IV) were used. Both tubes were 12.25 cm. in length.

By plotting stress[6] ($PR/2L$) against velocity gradient ($4V/\pi R^3$), curves are obtained which should be independent of the capillary dimensions, provided that: (1) each element of the material moves in a straight line parallel to the tube walls; (2) the material in contact with the wall is at rest with respect to it; and (3) the velocity gradient has a unique value for each value of shearing stress (cf. Schofield (7)). For true fluids the curves are linear, and pass through the origin.

It has been shown (8) that for certain pastes, the second and third conditions above do not hold, owing to anomalous flow near the tube walls. Moreover many materials, although obeying these three conditions, show a decrease in viscosity as stress increases, giving either a curvilinear flow-

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fall for a given tube and sphere remain proportional to the viscosities. Moreover, since in the above experiment the ratio r/R is the same in both cases, it is true to say that in so far as Ladenburg's approximations are applicable, the times of fall for the two balls will bear a ratio equal to the ratios of the squares of their diameters. Corrections due to the effect of the end of the tube (which cannot be regarded as anything like infinitely long in practice) are not large, and may be neglected for the purpose of the above experiments.

For a further discussion on this subject see Hatschek's Viscosity of Liquids, p. 33 (G. Bell and Sons, Ltd., London, 1928), and Barr's Viscometry, p. 171 (Humphrey Milton, London, 1931).

[5] Paine, Gertler, and Lothrop have already shown that certain (non-thixotropic) honeys show a slight fall in viscosity with increasing stress. A Bingham-Green plastometer was used.

[6] P is the pressure, R is the tube radius, L is the tube length, and V is the flow in cubic centimeters per second.

curve, or a curve which, although straight at high stresses, does not extrapolate to the origin (6).

It is clear from figure 1 that the sample of stirred heather honey (sol) shows no appreciable anomaly of the first type, but that, although approximating closely to a true fluid (especially at 30°C.), there is a small but significant tendency for viscosity to rise at low stresses (though this is not great enough to be observed in the experiment shown in table 2).

There is no evidence of a sharp yield value.

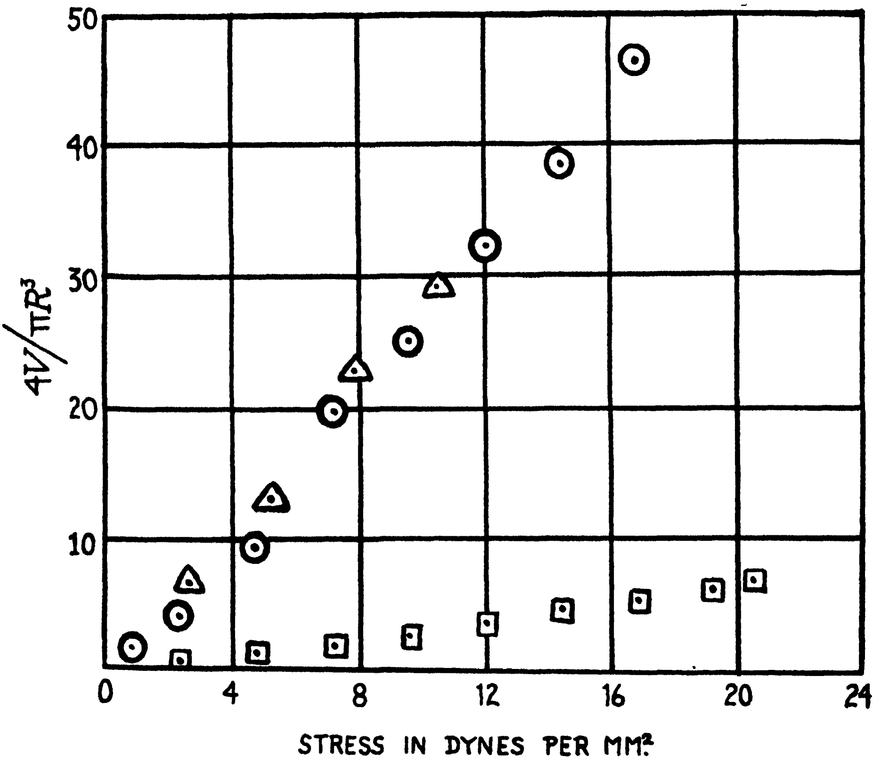

FIG. 1. FLOW CURVES FOR HEATHER HONEY

⊙ Capillary II, 30°C. △ Capillary IV, 30°C. ⊡ Capillary II, 15°C.

At 30°C. sample Y shows a viscosity at high stresses of about 37 C.G.S. units, and at 15°C. of approximately 300 C.G.S., though at 15°C. it is not certain that all thixotropic structure was really destroyed by shearing. Such a high viscosity brings the experiment rather near the limits of applicability of the plastometer.

DISCUSSION

Heather honey "gel" shows "rigid" properties in the sense that at low stresses, rapidly applied, the viscosity of the system is so high that it may be said to behave as an elastic solid, but there is no marked yield value—i.e., the elastic limit is not sharp. The change which takes place when the gel is broken up by stirring is a continuous one, involving a fall in viscosity and an increasing approximation to a truly fluid condition, but even a vigorously stirred sample shows signs of viscosity increase at very small stresses. The data are not adequate to specify just how sharp this change in viscosity may be, but there is certainly no well-defined yield value. A semiquantitative measure of thixotropy may be obtained by timing the fall of a steel ball through a sample of honey which has been left to stand overnight, disintegrating the gel by stirring with a perforated metal disk, and then immediately timing a second ball of the same size. Under fixed conditions, the ratios of the times of fall for heather honey before and after stirring show values of from about 5 to 200,[7] as compared with unity for Golden Syrup, and approximately unity for ordinary clover honey. If standardized conditions of temperature, size of vessel and balls, etc., are used, this should prove a useful test for deciding whether a sample is to be rejected on account of high moisture content, which in a normal honey would be an indication of "unripeness" and might lead to its subsequent spoiling by fermentation, or whether it is to be excused on the ground of its heather origin.

SUMMARY

Experiments are described on the behavior of heather honey under shearing, both in its undisturbed ("gel") and stirred ("sol") forms. In both cases, the viscosity increased at low stresses, but in neither case was there found any sharp elastic limit (yield value). The sol form showed (considering its very high viscosity) only a very small deviation from truly fluid behavior.

A simple viscometric test is described to characterize honeys having thixotropic properties. This test should prove of use in deciding whether excess water in a honey is caused by unripeness, or is natural, owing to its heather origin.

The author is indebted to Mr. D. A. Morland of the Apiculture Section of the Entomology Department of the Rothamsted Experimental Station for bringing to his notice the need for this investigation, and for advising him in the selection and description of the honeys tested.

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[7] Not many samples have yet been tested, and it is possible that further tests will show a still larger range of values.

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THE PHYSICAL AND CHEMICAL RELATIONS IN FLUID PHASE HETEROGENEOUS REACTION[1]

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In reaction between two phases, two factors *a priori* determine the overall measured rate of reaction. The first is the rate of chemical reaction at the interface; the second is the rate of transport of reactant, or product of reaction, to or from the interface. For heterogeneous reaction in which one or both phases are fluid, the transport takes place between the interface and the point of measurement.

In the present work, dealing with the fluid–fluid or fluid–solid heterogeneous reaction, a quantitative relationship is derived for the measured rate as a function of the chemical reaction rate and rate of physical transport. No arbitrary postulates as to mechanism are made. The results follow in the first place from a solution of the diffusion equation with chemical reaction at the interface constituting one of the boundary conditions. In the second place, diffusion as a mode of transport is generalized to include transport due to stirring or other type of agitation.

THE NERNST THEORY

In 1904, Nernst (21, 2) proposed a theory of heterogeneous reaction which has been referred to widely. In this theory certain assumptions are made as to the chemical and physical factors of the liquid–solid heterogeneous reaction. On the chemical side, reaction is supposed to be infinitely rapid, owing to an "infinite force" at the boundary. On the physical side, a stationary liquid film is supposed to exist through which diffusion into the main body of the stirred liquid takes place. For the solution of a solid, or for reaction between a solid and a solution, the adhering film at moderate rates of stirring is calculated to be 20 to 50 microns thick (2, 29).

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Regarding the chemical aspect of the Nernst theory, there is no reason for supposing that the rate of heterogeneous chemical reaction is "infinite." In other words, not all collisions of the reacting molecules will be expected to be fruitful; rather, an activation energy should be required, as for homogeneous reaction. In many cases, no doubt the second phase will exert a catalytic effect on the rate, but our knowledge of heterogeneous catalysis leads us to expect that a catalytic effect of the second phase, if and when it exists, would hardly be complete.

Regarding the physical aspect of the Nernst theory, experimental evidence strongly contradicts the possible existence of a stationary film. Contrasted with the Nernst film of 20 to 50 microns thickness, microscopic observation indicates a thickness of any possible film of less than 0.4μ (26); solution of a fine sediment indicates the possibility as less than 0.2μ (23); flow through capillaries less than 0.03μ (3); reaction in the presence of a monomolecular fatty acid less than 0.0025μ, or 25A.U. (20); while ultramicroscopic examination of water flowing slowly in pipes shows that, though the flow is axial, motion in all three directions persists right up to the surface (10).

The evidence of sedimentation may be considered in some detail. It has been found (23) that the volume of a coarse sediment consisting of 100-micron particles is the same before as after centrifuging, and equal approximately to the value common to all particle sizes after centrifuging. The coarse particles in the normally settled state are therefore densely packed and touching. The force necessary to displace completely any possible aqueous film surrounding the particles is merely that of gravity acting on a 100-micron particle, or a compressive force of 20 dynes per square centimeter for a particle of density 3. However, with water stirred at the moderate linear rate of 50 cm. per second, the forces are much greater. The tangential shearing stress tending to displace any possible film of, say, 25 microns thickness, is ten times as great, or 200 dynes per square centimeter. If the flow is directed toward the surface of the solid, the compressive stress is two hundred and fifty times as great, or 5000 dynes per square centimeter. Therefore it is impossible that a stationary film could exist in the presence of the forces evoked by ordinary stirring, a result that agrees with the other evidence already cited.

In most liquid-phase heterogeneous reactions the chemical effect is obscured, though only superficially, by conditions of physical transport. However, in many cases the chemical effect predominates, as shown in the following results: (a) The non-dependence of rate of reaction on rate of stirring, as for rate of solution of glass in alkali (25), of metals in acid (5), of olefins in sulfuric acid (9), of mineral sulfides in dilute sulfuric acid (24), of crystallization from supersaturated solution (19), of hydrolysis and saponification (11); (b) the frequent wide difference in rate of solution of certain of the crystalline faces of the self-same substance (22, 30); (c) a temperature coefficient appreciably greater than that for diffusion (1, 5, 18). The Nernst theory, which concentrates all attention on a hypothetical and apparently non-existent film, naturally has no explanation for these results.

On the contrary, these results and the more general facts of the heterogeneous reaction are accounted for in the relationships to be derived, which are founded simply on known physical and chemical laws.

RATE OF REACTION WITH TRANSPORT BY DIFFUSION

Let a plane solid of area F react with a prism of quiescent solution[3] of depth L, of area equal to that of the solid, and initial concentration c_0. In the body of the solution, the ordinary diffusion relation (equation 1), in which D is the diffusion coefficient, is obeyed.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

Out of all the molecules in solution, only those in the immediate neighborhood of the solid–fluid interface are in a position to make impact with the solid surface. For a gas, for instance, by kinetic theory out of all molecules which are three mean free paths distant from the interface, less than 1 per cent will strike the surface on their next collision. For a solution, the reacting molecules probably will be confined to those within one or two molecular distances from the solid surface. For both gas and solution the number of impacts per second is proportional to concentration, c, in the neighborhood of the interface. The number of gram-moles, m, reacting per unit area per unit time is proportional to the number of impacts and is given by equation 2, in which k is the specific reaction velocity constant.

$$\frac{1}{F}\frac{\partial m}{\partial t} = kc \tag{2}$$

The rate at which dissolved molecules disappear by reaction at the solid surface equals the rate at which they diffuse from the neighborhood of the interface to the interface. Therefore, by definition of diffusion and by equation 2,

$$D\frac{\partial c}{\partial x} = -kc \tag{3}$$

at $x = L$.

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[3] With partial pressure replacing concentration, the same derivation applies to reaction between a gas and solid, or gas and solution, provided it is of the first order.

At the surface of the solution,

$$\frac{\partial c}{\partial x} = 0 \tag{4}$$

at $x = 0$.

The solution of equation 1 with the boundary conditions imposed by equations 3 and 4 and the condition that $c = c_0$ when $t = 0$ is analogous to the solution of the equation for the radiating sphere in the theory of heat conduction (12). The concentration at point x and time t is found to be

$$c = c_0 \sum_{1}^{\infty} B_m \, e^{-\frac{D}{L^2}\beta_m^2 t} \cos \frac{\beta_m}{L} x \tag{5}$$

β_m is given by equation 6 and B_m by equation 7.

$$\beta_m \tan \beta_m = \frac{kL}{D} \tag{6}$$

$$B_m = \frac{4 \sin \beta_m}{2\beta_m + \sin 2\beta_m} \tag{7}$$

As a rule interest will be centered in the average concentration, $\bar{c}$, throughout the solution. $\bar{c}$ is obtained by integrating equation 5 between 0 and L, and dividing by L. There is thus obtained

$$\bar{c} = \bar{c}_0 \sum_{1}^{\infty} \bar{B}_m e^{-\frac{D}{L^2}\beta_m^2 t} \tag{8}$$

In equation 8 β_m is given by equation 6 as before. $\bar{B}_m$ is however now defined by equation 9 as follows:

$$\bar{B}_m = \frac{4\sin^2 \beta_m}{(2\beta_m + \sin 2\beta_m)\,\beta_m} \tag{9}$$

Having determined $\bar{c}$ against t, β_m may be calculated by equations 8 and 9. Knowing β_m, the chemical reaction velocity constant k, which is the variable of interest, is then obtained from equation 6.

NUMERICAL SOLUTION OF EQUATION 8

To simplify the calculation by equations 8, 9, and 6 of the chemical velocity constant k, table 1 has been constructed. This gives the values of the first two terms in equation 8,

$$\bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} \qquad \text{and} \qquad \bar{B}_2 e^{-\frac{D}{L^2}\beta_2^2 t}$$

(also β_1 and β_2), for values of kL/D from 0 to ∞ and for Dt/L^2 up to 1.6.

It is seen from table 1 that for Dt/L^2 sufficiently great, the series of equation 8 converges very rapidly. For $Dt/L^2 = 0$, the second term is at the most 11 per cent of the first, while the sum of the second and all remaining terms is at the most 22 per cent of the first. For $Dt/L^2 = 0.1$, these figures become respectively 1.8 per cent and probably less than 3.6 per cent, while for $Dt/L^2 = 0.2$, they become 0.4 per cent and probably less than 0.8 per cent, respectively. For an error smaller than 1 per cent, all terms but the first may therefore be neglected, provided $Dt/L^2 \geqq 0.2$.

Table 1 is made use of as follows. At a given value of Dt/L^2, one proceeds down the column to a value of

$$\bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} \left(\text{or } \bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} + \bar{B}_2 e^{-\frac{D}{L^2}\beta_2^2 t}\right)$$

equal to the known value of $\bar{c}/\bar{c}_0$. The desired quantity kL/D is then obtained by reading across to the first column. For L one may substitute V/F, the ratio of volume of the vessel to surface area of the solid. In view of the fact that $\bar{c}$ is an average concentration, the same substitution appears possible when the vessel is non-prismatic. Knowing the diffusion coefficient and depth of the vessel, k is readily obtained from the known value of kL/D.

RELATION TO THE USUAL FIRST-ORDER EQUATION

The course of most fluid-phase heterogeneous reactions, it has been found, is represented by the usual first-order reaction velocity equation. The equation is, for the case of reaction between a solid and solution,

$$\frac{d\bar{c}}{dt} = -K\frac{F}{V}\bar{c} \tag{10}$$

On integration equation 10 gives

$$K = -\frac{2.303}{t}\frac{V}{F}\log\frac{\bar{c}}{\bar{c}_0} \tag{11}$$

In equation 11 K is the measured reaction velocity constant, V the volume of the vessel, and F the surface of the solid.

Under the condition that all terms but the first may be neglected, that is for $Dt/L^2 \geqq 0.2$ for an error smaller than 1 per cent, equation 8 assumes the form of a first-order reaction velocity equation, and, with V/F substituted for L, may be written

$$\frac{D}{L}\beta_1^2 = -\frac{2.303}{t}\frac{V}{F}\log\frac{\bar{c}}{\bar{B}_1\bar{c}_0} \qquad \frac{D}{\mathrm{L}^2}t \geqq 0.2 \tag{12}$$

$\bar{B}_1$ in equation 12, as shown in the fourth column of table 1, is close to unity, especially for those values of kL/D that are themselves less than unity (which values it will be seen are of most interest).

TABLE 1

Numerical solution of equation 8

kL/D	β_1	β_2	$\frac{D}{L^2}t = 0.0$		$\frac{D}{L^2}t = 0.1$		$\frac{D}{L^2}t = 0.2$		$\frac{D}{L^2}t = 0.4$		$\frac{D}{L^2}t = 0.8$	$\frac{D}{L^2}t = 1.6$
			$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$	$\bar{B}_{2e}^{-\frac{D}{L^2}\beta_2^2t}$	$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$	$\bar{B}_{2e}^{-\frac{D}{L^2}\beta_2^2t}$	$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$	$\bar{B}_{2e}^{-\frac{D}{L^2}\beta_2^2t}$	$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$	$\bar{B}_{2e}^{-\frac{D}{L^2}\beta_2^2t}$	$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$	$\bar{B}_{1e}^{-\frac{D}{L^2}\beta_1^2t}$
0.00	0.000	3.14	1 000	0.000	1.000	0 000	1 000	0 000	1 000	0 0000	1 000	1.000
0.25	0.480	3 22	0.999	0.001	0 976	0.000	0 954	0 000	0 911	0 0000	0 831	0.691
0.50	0.655	3 29	0 995	0.004	0 954	0 001	0 914	0 000	0 839	0.0001	0.708	0.502
1.00	0.860	3.43	0 990	0.013	0 918	0.004	0 854	0.001	0.736	0 0001	0 547	0.304
1.50	0.989	3.55	0 973	0 022	0 882	0 006	0 800	0.002	0 658	0 0001	0 445	0.204
2.00	1.079	3.65	0.956	0.032	0 852	0 008	0 758	0 002	0 600	0 0002	0.379	0.149
4.00	1.265	3.94	0 928	0 057	0 789	0 012	0 674	0 003	0.490	0 0001	0.259	0.072
8.00	1.398	4.22	0.885	0.080	0 728	0 013	0.600	0.002	0 406	0 0001	0.186	0 039
16 00	1.479	4.44	0 854	0.089	0 688	0.012	0 552	0 002	0 357	0 0000	0.150	0.026
32.00	1.522	4 57	0 834	0 091	0 661	0 011	0 524	0 001	0.330	0 0000	0.131	0 021
∞	1.562	4.70	0 819	0.090	0 642	0 010	0 503	0 001	0 309	0 0000	0 117	0.016

With $\bar{B}_1$ assumed nearly equal to unity and $Dt/L^2 \geqq 0.2$, the right-hand sides of equations 11 and 12 are substantially equal. Therefore

$$K = \frac{D}{L}\beta_1^2 \qquad \begin{matrix} \bar{B}_1 \doteq 1 \\ \\ \dfrac{Dt}{L^2} \geqq 0.2 \end{matrix} \tag{13}$$

Equation 13 is exact, subject to the stipulated conditions, which are easily satisfied. In this equation K, the measured velocity constant, is given indirectly as a function of k, the true chemical rate constant, D, the diffusion coefficient, and L (or V/F), the depth of the vessel.

EXPLICIT SOLUTION FOR MEASURED VELOCITY CONSTANT

β_1^2 in equation 13 is determined by equation 6. The latter is a transcendental expression which does not allow of explicit solution for β_1^2. In table 1 are given the indirectly solved values of β_1, which are seen to extend over a narrow range, for kL/D from 0 to ∞.

It will be highly desirable (especially for the purpose of later generalization) that β_1^2 be expressed explicitly if possible, even though an approximation be introduced thereby. From equation 6 it is seen that β_1^2 is a function of kL/D. In any substitution for β_1^2, it is necessary that β_1^2 be zero for kL/D zero, finite for kL/D infinite, and that there be numerical agreement at least over a certain range. It is proposed as meeting these conditions that β_1^2 be set equal to $(1 - e^{-kL/D})$. When the substitution is made, equation 13 becomes

$$K = D/L\,(1 - e^{-kL/D}) \tag{14}$$

Equation 14 is readily solved for the chemical rate constant k, giving

$$k = -2.303\,D/L \log(1 - KL/D) \tag{14$'$}$$

According to equation 14, when $k \geqslant D/L$, the measured rate constant K is determined by D/L. On the other hand when $k \leqslant D/L$, $K \doteq k$, or the measured rate constant is closely equal to the true chemical velocity constant.

To test the validity of the functional substitution for β_1^2, table 2 has been constructed comparing kL/D calculated from equation 14′ with the correct value of kL/D obtained from table 1, for different assumed values of KL/D, i.e. β_1^2 by equation 13. It is seen that kL/D varies over an infinite range, while the variation of KL/D is restricted to the narrow range 0.0 to 2.44. Agreement in the exact values of kL/D and values calculated from equation 14′ are within 10 per cent for KL/D less than 0.4, and within 35 per cent for KL/D less than 0.75. KL/D between 0 and

0.75 covers about one-third the total range in values of KL/D. However KL/D lying in the low range of values is most significant, because it is in the low range that k plays an important rôle in determining the magnitude of K. With increase in KL/D, the effect of k in determining the value of K becomes smaller and smaller compared to that of diffusion. Bearing this consideration in mind, the explicit approximation represented by equation 14 may be considered as fairly satisfactory. In the end, the approximation represented by equation 14 is intended not so much for pure diffusion as a mode of transport as for other modes of transport for which the validity appears to be more extended, as will shortly be discussed.

TABLE 2

kL/D, exact and as determined by equation 14′, against KL/D

KL/D	kL/D	
	Exact	Equation 14′
0.00	0.00	0.00
0.23	0.25	0.26
0.43	0.50	0.55
0.74	1.00	1.35
1.00	1.5	∞
2.44	∞	

RATE OF SOLUTION AND CRYSTALLIZATION

Solution or crystallization differs from simple chemical reaction just considered in that molecules simultaneously condense at and are liberated from the solid surface. The mole rate of condensation at the interface is given by equation 2. The mole rate of liberation of molecules from the surface is determined by the equilibrium condition that it equal the rate of condensation from the saturated solution, or kc_s. The rate of solution or of crystallization at the interface is the difference between the rate of condensation and of liberation, and is given by

$$1/F \frac{\partial m}{\partial t} = k(c_s - c) \tag{2'}$$

at $x = L$.

From this point the derivation is exactly analogous to that already considered ($c_s - c$ merely replacing c as variable), and the same final expression for K is obtained (equation 14).

GENERALIZED EQUATION FOR MEASURED VELOCITY CONSTANT

Transport of reactant or product of reaction will usually occur by modes independent of and in addition to diffusion. Concentration and convection currents are frequent natural accompaniments of the diffusion process. Artificial transport is secured by mechanical stirring, agitation, etc. These various modes of transport usually are much more effective than is diffussion itself. Unless they are taken into account, any relationship between the measured and the true chemical velocity constant can be only of very limited scope.

It is observed that D/L in equation 14 has the dimensions of a velocity. It may be defined therefore as the rate of group molecule transport by molecular diffusion, i.e., as the coefficient of transport by diffusion. An obvious extension of equation 14 is to replace the diffusion coefficient of transport, D/L, as simply a special case, by a general coefficient of transport, S. Equation 14 for the measured rate constant then becomes

$$K = S(1 - e^{-k/S}) \tag{15}$$

By analogy with equation 14 it may be expected that the limit of validity of equation 15 will be determined by the value of K/S. How close K/S may approach to unity before the equation palpably fails can not be told beforehand, and is to be answered only by experiment.

It may be noted at this point that with transport by mechanical stirring, the generalized equation held, within limit of error as seen below, practically for all values of K/S that were encountered. While an exact limit for K/S can not now be given, it appears that with transport by mechanical stirring the equation holds for K/S equal to 0.9 at least, and probably also for greater values.

TRANSPORT BY MECHANICAL STIRRING

In the measurement of liquid-phase heterogeneous reaction rate, the most common method of inducing molecule transport in the liquid is by mechanical stirring. The coefficient of transport obviously will increase with the rate of stirring. For fast reactions, which are determined by transport, Jablczynski (13) found that the rate varied approximately with the 0.85th power of the rate of stirring, while Van Name and Edgar (27) found the power to be 0.80. For the intermediate rates of solution and reaction considered below, the transport likewise is found to be proportional to the 0.8th power of the rate of stirring. Therefore, transport by diffusion being neglected against that effected by the stirring, the coefficient of transport S is given by

$$S = As^{0.8} \tag{16}$$

where s is the rate of stirring in R.P.M., and A a constant which depends on experimental conditions and on the physical properties of the fluid, namely the viscosity and the density.

The result for the exponent of s in equation 16 agrees with that found in heat transfer with fluid flow in pipes, where the transfer coefficient, as summarized by McAdams (17), varies with the 0.8th power of the rate of flow of fluid.[4]

It has been held (15, 16) that the rate of reaction varies with the first power of the rate of mechanical stirring. Although this result might obtain under exceptional stirring conditions, as in the combined gas-feed and mechanical stirring of Huber and Reid (11), it is contrary to the generally recognized result of an exponent less than unity. The occasional apparent linear dependence probably arises from the combination of inaccurate, insufficient, or non-uniform data with the fact that a plot of $y = x^{0.8}$ shows but small curvature.

King and Braverman (16), for instance, find that the rate of solution of a zinc specimen rotating axially in acetic acid becomes linear above a certain speed and up to 5500 R.P.M. Nevertheless their plot for zinc and hydrochloric acid shows continuous curvature throughout, and incidentally, as far as can be estimated from the plotted points, the plot for hydrochloric acid appears to be fitted tolerably well by equation 17 below. If any linearity existed it should have applied to the faster reaction with hydrochloric acid, rather than to the reaction with acetic acid. It is to be concluded that the apparent linear result with acetic acid is due probably to the entrance of some secondary effect with increased high-speed stirring, such as heating, vibration, vortices, or some other disturbing factor not present under uniform conditions.

Substituting, then, from equation 16 into equation 15, the following relationship connecting K and k with the rate of mechanical stirring is obtained:

$$K = As^{0.8}(1 - e^{-k/As^{0.8}}) \tag{17}$$

An apparent exponent of less than 0.8, in accordance with equation 17, is due to the progressive influence of the chemical reaction velocity on the measured rate constant. For instance, Brunner (2) considered that the rate of solution of benzoic acid in water was proportional to the two-thirds power of the rate of stirring. However, it will be seen below that the exponent for Brunner's data is 0.8 as usual, but the rate of solution is slow enough to affect measurably the value of K and thus to result in an apparent exponent of less than 0.8.

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[4] The film theory has also been widely carried over to heterogeneous heat transfer. Recently Kennard (14) has examined the atmosphere adjacent to a hot solid surface and found no evidence of any film. The case of heterogeneous heat transfer is analogous to that of heterogeneous chemical reaction, and the results obtained here apply also to heat transfer, K being redefined as the measured coefficient of heat transfer and k as the velocity constant of heat transfer at the interface. In view of an exponent of 0.8 for the fluid velocity, k would appear to be large against the coefficient of physical transport.

APPLICATION

In heterogeneous as in homogeneous chemical reaction one is interested in the value of the chemical reaction velocity constant, k. Separation of the physical and chemical factors that determine the measured constant K is secured in general by equation 15.

When the transport is effected by mechanical stirring, equation 17 applies. To determine k, it merely is necessary to evaluate A by measurement of K at different stirring speeds.

For the calculated value of k to be accurate, its contribution to the value of the measured constant K must be sufficiently great. In other words, K must be measured at sufficiently high stirring speeds. A criterion as to whether one is in a range of stirring speeds in which k exerts an appreciable influence on the magnitude of K is found in the ratio $K/s^{0.8}$. If this ratio decreases sufficiently with increase in stirring speed, the range of speeds is then proper to an accurate determination of k.

EXAMPLES

The oxidation of mercury by iodine in potassium iodide solution, measured by Van Name and Edgar (27) at different stirring speeds up to 300 R.P.M., is a reaction in which the decrease in the ratio $K_{\text{obsd.}}/s^{0.8}$ is so small that accurate determination of the true reaction constant k is not possible. The data for this reaction are given in table 3.[5] It is seen from column 3 that the decrease in the ratio with decrease in stirring speed is less than 2 per cent over the whole range of stirring speeds from 170 to 300 R.P.M.

However, a large proportion of the reactions that have been reported in the literature show a sufficiently rapid decrease of $K_{\text{obsd.}}/s^{0.8}$ with increase in stirring speed to permit application of equation 17. Reactions for which accurate data are available are the following: (a) Benzoic acid in water (30), (b) oxygen in water (4), (c) magnesium in 1/8 M hydrochloric acid (6), (d) thallium in 1/2 M nitric acid (8), (e) zinc in 0.02 M copper sulfate (7). These typical reactions are considered in tables 4 to 8 inclusive. In column 2 of these tables is shown the decrease in $K_{\text{obsd.}}/s^{0.8}$ with increase in s. In the third and fourth columns are shown $K_{\text{obsd.}}$ and the value of K calculated by equation 17 for assigned values of k and A.

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[5] In all examples, the author's value of the measured rate is recalculated where necessary so as to conform to the precise equation (11), or to its analogue, for $K_{\text{obsd.}}$. K and k are expressed in centimeters per minute.

For benzoic acid in water (table 4), the same value of k satisfies excellently the results of three different observers, though naturally the values of A differ for the different experimental conditions. The fifth column shows that there is no systematic deviation in the percentage difference between the calculated and observed values of K, the differences being positive and negative at random.

TABLE 3

Rate of oxidation of mercury by iodine in potassium iodide (27)

s IN R.P.M.	$K_{\text{obsd.}}$	$\frac{K_{\text{obsd.}}}{s^{0.8}} \times 10^3$
170	0.574	9.45
210	0.679	9.45
240	0.759	9.45
300	0.885	9 30

TABLE 4

Rate of solution of benzoic acid in water

$k = 0.157$

s IN R.P.M.	$\frac{K_{\text{obsd}} \times 10^3}{s^{0.8}}$	K_{obsd}	$K_{\text{calcd.}}$	PERCENTAGE DIFFERENCE
		$A = 0\ 00147(30)$		
3	2.18	0.0052	0.0035	+32
53	1.13	0.0270	0.0348	−29
122	1.10	0.0513	0.0618	−20
204	1.34	0.0943	0.0810	+14
365	1.00	0.1120	0.1015	+9
470	0.75	0.1030	0.1090	−6
		$A = 0\ 0011(1)$		
100	1.16	0.046	0.042	+8
450	0.67	0 088	0.096	−9
		$A = 0.0055(2)$		
144	2.20	0.118	0.121	−2.5
202	1.85	0.131	0.129	+1 5

The least accurate data are those for benzoic acid; this is reflected in the irregular decrease in $K/s^{0.8}$ for this reaction (table 4), contrary to that for the other reactions. The percentage difference averaged for all the experimental points for benzoic acid is ±13 per cent. The most accurate measurements appear to be those on the solution of zinc in copper sulfate (table 8). The average percentage difference is only ±1.2 per cent. For all the reactions the average difference is ±6.2 per cent.

Table 9 summarizes the values of k and A for the reactions considered. It is seen that k varies between 0.078 and 2.80, or over a thirty-five-fold range. The variation of A, from 1.1 to 12.0 × 10^{-3}, is more restricted.

TABLE 5

Rate of solution of oxygen in water (4)

$k = 2\ 06$; $A = 0.00177$

s IN R.P.M.	$\frac{K_{\text{obsd}}}{s^{0\ 8}} \times 10^3$	K_{obsd}	K_{calcd}	PERCENTAGE DIFFERENCE
60	1.82	0 0480	0 0462	+3.7
93	1 64	0.0621	0.0639	−2.9
120	1.63	0 0749	0.0749	0
145	1.55	0.0835	0.0844	−1.1
180	1 54	0 0977	0.0942	+3.6

TABLE 6

Rate of solution of magnesium in 1/8 M hydrochloric acid (6)

$k = 2\ 80$; $A = 0\ 010$

s IN R.P.M.	$\frac{K_{\text{obsd}}}{s^{0.8}} \times 10^3$	$K_{\text{obsd.}}$	$K_{\text{calcd.}}$	PERCENTAGE DIFFERENCE
50	15.7	0.36	0.23	+33
100	10 5	0.41	0 40	+3
200	9 7	0 67	0.68	−1
400	7 9	0 95	1.08	−14
750	7 2	1.43	1.50	−5
855	7 7	1 72	1 59	+8

TABLE 7

Rate of solution of thallium in 1/2 M nitric acid (8)

$k = 0.078$; $A = 0\ 0044$

s IN R.P.M.	$\frac{K_{\text{obsd}}}{s^{0.8}} \times 10^3$	K_{obsd}	$K_{\text{calcd.}}$	PERCENTAGE DIFFERENCE
32	2.96	0.0474	0.0472	+0 4
74	1.84	0.0578	0.0596	−3.1
120	1.42	0 0654	0.0649	+0.8
193	1.00	0 0678	0.0688	−1 5
454	0 55	0 0733	0.0731	+0.3

THE FORM OF THE CURVE

In figure 1, $K_{\text{calcd.}}$ is plotted against R.P.M. for reactions a to e. The experimental points fall irregularly on either side of the curves. The curves all are concave downward. The degree of curvature shows considerable variation. For reaction b it is slight, the curve appearing almost as a straight line; for reaction d it is very pronounced up to 150 R.P.M., after which the curve becomes asymptotic. For the other reactions the curvature is intermediate.

In the same range of stirring speeds, the form of the curve is determined by the ratio k/A shown in table 9. For reaction d the ratio is only 0.02 $\times 10^3$, and the curvature is high; for reaction b the ratio is 1.16 $\times 10^3$, and the curvature is very small. Reactions a and e have about the same intermediate ratio and curvature.

TABLE 8

Rate of solution of zinc in 0.02 M copper sulfate (7)

$k = 1.50$; $A = 0.012$

s IN R.P.M.	$\frac{K_{\text{obsd.}}}{s^{0.8}} \times 10^3$	$K_{\text{obsd.}}$	$K_{\text{calcd.}}$	PERCENTAGE DIFFERENCE
54	13.8	0.336	0.292	+13.0
94	11.5	0.436	0.440	−0.9
295	8.8	0.836	0.834	+0.2
500	7.0	1.007	1.005	+0.2
600	6.4	1.061	1.055	+0.6
680	5.6	1.028	1.088	−5.8

TABLE 9

Summary of values of chemical reaction velocity constant, k, and of A

REACTION	k	$A \times 10^3$	$\frac{k}{A} \times 10^{-3}$
	cm. per min.		
(a) Benzoic acid in water (30)	0.157	1.47	0.11
Benzoic acid in water (1)	0.157	1.10	0.14
Benzoic acid in water (2)	0.157	5.50	0.03
(b) Oxygen in water (4)	2.06	1.77	1.16
(c) Magnesium in 1/8 M hydrochloric acid (6)	2.80	10.0	0.28
(d) Thallium in 1/2 M nitric acid (8)	0.078	4.4	0.02
(e) Zinc in 0.02 M copper sulfate (7)	1.50	12.0	0.12

TEMPERATURE COEFFICIENT

By equation 17 the temperature coefficient of K is determined by that of k and of A. A varies with temperature chiefly through its dependence on the viscosity. By analogy with the heat transfer coefficient (based simply on the Reynold's number and considered as a coefficient of transport), A should be equal to $A'\phi^{0.8}$, where ϕ is the fluidity. This result accords with the measurements of the temperature coefficient of zinc in 0.02 M copper sulfate at 100 R.P.M. (reaction e) by Centnerszwer and Heller (7). These authors find $K_{25}/K_0 = 1.83$, while $\phi_{25}/\phi_0 = 1.97$ and $\phi_{25}^{0.8}/\phi_0^{0.8} = 1.72$; also $K_{50}/K_{25} = 1.47$, while $\phi_{50}/\phi_{25} = 1.64$ and $\phi_{50}^{0.8}/\phi_{25}^{0.8} = 1.48$.

On the other hand, the results of King and Braverman (16) and Van Name and Hill (28) for rapid reactions in which alcohol and cane sugar have been added to the solutions, indicate that the measured constant varies as the first power of the fluidity. If these measurements are accurate, and if a possible effect of added reagent on the chemical velocity constant is neglected, then $A = A'\phi$.

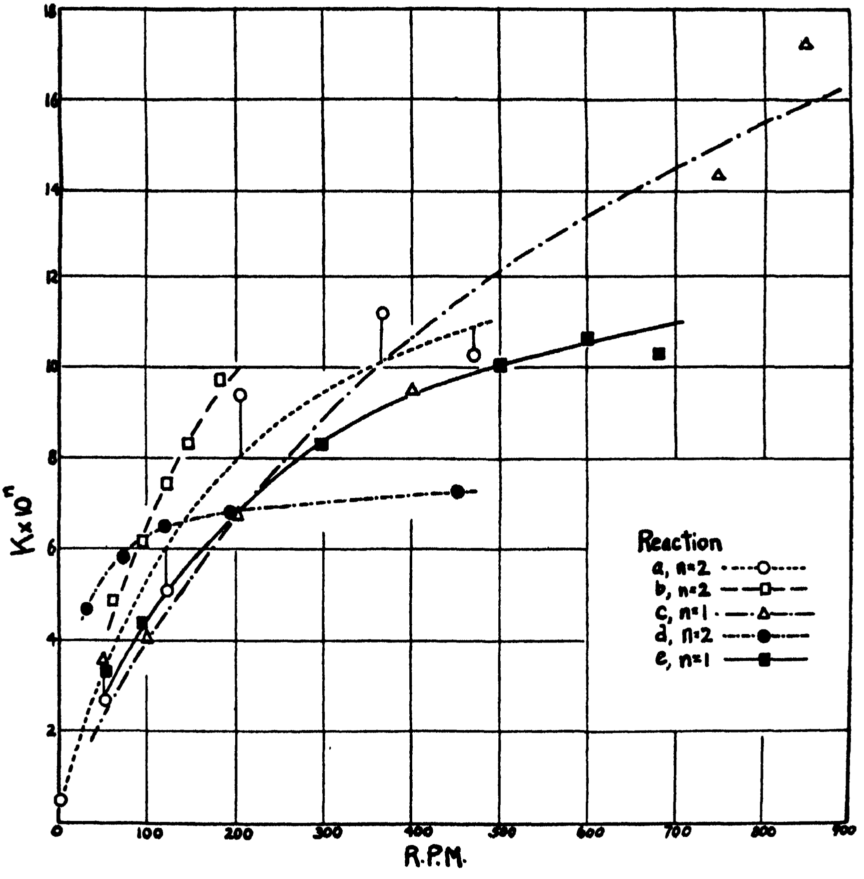

FIG. 1. RELATION OF MEASURED RATE CONSTANT TO SPEED OF STIRRING

In any case

$$k_{t+10}/k_t > \varphi_{t+10}^{0.8\,(\text{or }1)}/\varphi_t^{0.8\,(\text{or }1)}.$$

Applying this inequality to equation 17, and remembering that in the limit $K = k$, the following relation is found to hold

$$k_{t+10}/k_t > K_{t+10}/K_t > \varphi_{t+10}^{0.8\,(\text{or } 1)}/\varphi_t^{0.8\,(\text{or } 1)} \tag{18}$$

The inequality 18 states that the measured temperature coefficient will lie between the coefficient of viscosity and of true chemical reaction. This is the result that has been found generally, with leanings toward viscosity coefficient or chemical coefficient depending on the ratio $k/As^{0.8}$.

SUMMARY

1. The postulates of the Nernst theory of fluid-phase heterogeneous reaction are criticized. In particular, independent experimental evidence is brought forward against the assumed existence of a stationary film.

2. In this paper, the measured rate of fluid-phase heterogeneous reaction is considered to be simply the resultant of two simultaneous processes —of chemical reaction at the interface and of physical transport to or from the interface—with no arbitrary assumptions as to mechanism.

3. To determine the functional relationship between the chemical and physical factors, the ordinary diffusion equation has been solved with one of the boundary conditions that of first-order reaction at the interface. The solution permits accurate calculation of the true chemical rate constant, knowing the value of the diffusion coefficient and the dimensions of the vessel.

The solved equation is brought into relation to the first-order rate equation that is usually found to apply. An implicit, and finally an explicit equation, connecting the usual measured rate constant, true chemical velocity constant, and diffusion coefficient are deduced, and the range of validity indicated.

4. By regarding diffusion as a special mode of molecule transport, the explicit equation is generalized to the following expression for the measured rate constant K,

$$K = S(1 - e^{-k/S})$$

where k is the chemical reaction velocity constant, and S the coefficient of physical transport of reactant or product of reaction to or from the interface.

5. For transport by mechanical stirring of the liquid phase, it is found that $S = As^{0.8}$, where A is a constant and s is the stirring speed. Exponent 0.8 agrees with that commonly found for the fluid velocity in the expression for the coefficient of heat transfer.

6. The values of K, measured as a function of the stirring speed for five typical reactions, are compared with the calculated values, and excellent

agreement obtained. k varies thirty-five-fold between 0.078 and 2.80 for the different reactions, while A lies between 1.1 and 12×10^{-3}.

7. The form of the curve of K against R.P.M. is considered in terms of the ratio k/A.

8. It is shown that the temperature coefficient of K must lie between the chemical coefficient and the viscosity coefficient, depending on the ratio $k/As^{0.8}$.

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SOLUBILITIES OF SOME STRYCHNINE BENZOATES

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During the use of some strychnine benzoates in a series of toxicological and pharmacological experiments (1), it became necessary to determine their solubilities in water at 20°C. It was decided to make like determinations at other temperatures, and the results of this investigation are reported in the present communication.

For the determination of the solubilities up to 60°C., a constant temperature bath, capable of being regulated to ±0.05°, was used. The strychnine salt was placed in a Pyrex test tube with about 30 cc. of water, and the tube was sealed. For the lower temperatures the mouth of the test tube was closed by sealing in the flame; for the higher temperatures pure gum rubber stoppers were used. A number of tubes were fastened to a frame, which in turn was connected to a mechanical shaker. The tubes were allowed to remain in the bath for from thirty-six to forty-eight hours.

For the determination of solubilities at the higher temperatures, an excess of the strychnine salt in distilled water was brought to the boiling point and then allowed to cool to the desired temperature. The tube containing the solution was allowed to remain in a constant temperature bath at this temperature for at least thirty minutes. In order to obtain a temperature of 95°C., since water at this altitude boils below this temperature, a small amount of sodium chloride was added to the water in the water bath. The tubes containing the strychnine salts in water were placed in this boiling solution. The bath used was a large Erlenmeyer flask. Most of the water which evaporated condensed and ran back in the flask. If the thermometer kept in the salt solution indicated that the temperature was greater than 95°C., a new salt solution was used. In every case the tubes were frequently agitated.

After the salts had remained in contact with the water at the desired temperature for the required length of time, the tubes were removed to a constant temperature air oven regulated to the same temperature. With pipettes heated to this same temperature, 25 cc. of the solution was removed from each tube, placed in a weighed platinum dish, and evaporated to dryness on the water bath. The dish was then placed in an air oven and dried to constant weight at 100°C. The grams of the strychnine compound present in 100 cc. of solution were calculated. The results showing the different solubilities are presented in table 1. From the data in this table it may be noted that a number of the compounds gave rather high solubility values in water. As a rule the ortho compounds gave the highest values, but this was not true for the nitro, methyl, and amino compounds. In these three compounds the meta form showed the greatest solubility. The compounds with the benzoic acids having more than one substituted group gave, as a rule, very low solubility values. The strychnine diiodosalicylate was almost insoluble in water at all temperatures.

TABLE 1

Solubilities of some strychnine benzoates

STRYCHNINE SALT	GRAMS OF SALT PER 100 CC. OF SOLUTION AT THE GIVEN TEMPERATURES						
	T = 20°C.	*T* = 30°C	*T* = 40°C.	*T* = 50°C.	*T* = 60°C.	*T* = 75°C.	*T* = 95°C.
Benzoate	0.433	0.578	0.784	1.156	1.607	2.311	3.460
o-Chlorobenzoate	1.783	1.995	2.211	2.770	3.410	4.798	10.725
m-Chlorobenzoate	0.176	0.229	0.344	0.509	0.669	0.944	1.376
p-Chlorobenzoate	0.264	0.302	0.330	0.425	0.551	0.688	1.158
o-Bromobenzoate	1.063	1.204	1.410	1.846	2.470	3.818	6.571
m-Bromobenzoate	0.092	0.115	0.141	0.201	0.402	0.576	0.835
p-Bromobenzoate	0.211	0.244	0.299	0.351	0.528	0.744	0.915
o-Iodobenzoate	0.526	0.582	0.653	0.768	1.122	1.514	2.116
p-Iodobenzoate	0.167	0.195	0.229	0.341	0.475	0.606	0.840
o-Nitrobenzoate	0.521	0.621	0.724	0.928	1.320	1.970	3.140
m-Nitrobenzoate	0.447	0.565	0.706	0.896	1.359	2.452	4.138
p-Nitrobenzoate	0.183	0.222	0.266	0.328	0.467	0.698	0.970
o-Hydroxybenzoate	0.250	0.297	0.402	0.606	0.964	1.470	2.500
m-Hydroxybenzoate	0.179	0.185	0.335	0.432	0.562	0.872	1.517
p-Hydroxybenzoate	0.149	0.188	0.241	0.339	0.517	0.875	1.432
o-Methylbenzoate	0.519	0.634	0.984	1.331	1.958	2.807	4.142
m-Methylbenzoate	0.869	0.992	1.181	1.688	2.350	3.856	7.765
p-Methylbenzoate	0.560	0.578	0.625	0.828	0.931	1.250	1.808
o-Aminobenzoate	0.297	0.378	0.462	0.710	0.984	1.590	2.602
m-Aminobenzoate	1.092	1.204	1.437	2.107	2.971	4.786	7.963
p-Aminobenzoate	0.371	0.652	0.986	1.324	2.046	3.586	7.136
3,5-Dinitrobenzoate	0.136	0.163	0.197	0.271	0.384	0.599	0.951
2,4-Dinitrobenzoate	0.249	0.298	0.389	0.557	0.821	1.230	1.610
2,4,6-Trinitrobenzoate	0.075	0.098	0.116	0.165	0.273	0.450	0.717
5-Iodosalicylate	0.037	0.045	0.057	0.079	0.126	0.215	0.374
3,5-Dinitrosalicylate	0.025	0.041	0.063	0.088	0.116	0.422	1.064
Diiodosalicylate	0.020	0.023	0.031	0.032	0.046	0.071	0.127

SUMMARY

The solubilities in water at different temperatures have been determined for twenty-seven strychnine benzoates.

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THE CONCENTRATION CHANGES AT MEMBRANES AND THE ELECTROÖSMOTIC MEMBRANE POTENTIALS

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In a previous paper (2) I have derived from Gouy's theory of a "diffuse" double layer, formulas for the transport numbers of ions in electroösmotic systems. They permit us to calculate both the concentration changes and the potential difference at diaphragms through which an electroösmotic current is driven.

At first, however, we will deduce the expressions for the transport numbers and bring these to a more convenient form. For a capillary slit, h cm. high and l cm. wide, we have for the fraction of the current carried by the anion

$$\begin{aligned} i_a &= \nu FCv_a hlX + 2\nu FChX \int_0^{l/2} v_a(N_a - 1)\,dx - 2\nu FCh \int_0^{l/2} uN_a\,dx \\ &= \nu FCv_a hlX + 2\nu FChX \int_0^{l/2} v_a(N_a - 1)\,dx - 2\nu FCh \int_0^{l/2} u\,dx \qquad (1) \\ &\quad - 2\nu FCh \int_0^{l/2} u(N_a - 1)\,dx \end{aligned}$$

where X is the field strength in the capillary, ν valency of both ions, F the Faraday constant, C the concentration of anion (in gram-ions per cubic centimeter) in the middle of the slit, N_aC this concentration at the distance x from the slit wall, v_a the mobility of the anion (centimeters per second per 300 volts per centimeter), u the electroösmotic velocity. A proof of this equation is to be found in my previously mentioned paper. In the same paper expressions were given for u and N_a; after integrating and with regard to the relation $2h\int_0^{l/2} u\,dx = V$, where V is the total liquid flow through the slit, we have, if the capillary is not too narrow,[2]

$$i_a = \nu FChX \left\{ v_a l - \frac{8v_a}{\alpha(A + 1)} - \frac{V}{hX} - \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A + 1} - \frac{1}{2}\ln\frac{A + 1}{A - 1}\right]\right\} \qquad (2)$$

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[2] In this case we can write (see equation 11 of reference 2)

$$u = X\frac{4\nu FC}{\eta\alpha^2}\left(\ln\frac{A + 1}{A - 1} - \ln\frac{Ae^{\alpha x} + 1}{Ae^{\alpha x} - 1}\right)$$

where η is the viscosity,

$$\alpha = \frac{2\nu F\sqrt{2\pi C}}{\sqrt{DRT}} \tag{3}$$

D the specific inductive capacity,

$$A = \frac{e^{-\frac{\nu F}{2RT}\zeta} + 1}{e^{-\frac{\nu F}{2RT}\zeta} - 1} \tag{4}$$

ζ being the electrokinetic potential difference.

The expression for the fraction of the current carried by the cation is like equation 2,

$$i_c = \nu FChX\left\{v_c l + \frac{8v_c}{\alpha(A-1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A-1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{5}$$

The transport numbers are evidently $\frac{i_c}{i_c + i_a}$ and $\frac{i_a}{i_c + i_a}$, as we suppose that the solution contains two kinds of ions only.

We consider now (the "pinch effect" (3, 4) being neglected) the cross section of the slit at the flow entrance. Suppose that the liquid is positive relative to the negatively charged slit wall and moves to the cathode. If the field strength outside the slit be X_0, the amount of electricity brought by the cations per second to the slit entrance will be

$$i_c^0 = \nu FCv_c hlX_0$$

The amount of electricity going away with the cation is i_c. The accumulation of cation charge per second is therefore

$$i_c^0 - i_c = \nu FC\,v_c hl(X_0 - X) - \nu FChX \left\{\frac{8v_c}{\alpha(A-1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A-1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{6}$$

In an analogous manner we find for the accumulation of the anion charge

$$i_a - i_a^0 = -\nu FCv_a hl(X_0 - X) - \nu FChX \left\{\frac{8v_a}{\alpha(A+1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A+1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{7}$$

In the stationary state these two expressions must be equal, because otherwise a continual increase of free electric charge should take place. From the equation $i_c^0 - i_c = i_a - i_a^0$ we obtain

$$(v_c + v_a)\,l(X_0 - X) = X\cdot\frac{8}{\alpha}\left[\frac{v_c}{A-1} - \frac{v_a}{A+1} + \frac{8\nu FC}{\eta\alpha^3}\cdot\frac{1}{A^2-1}\right] \tag{8}$$

whence

$$X_0 - X = X \cdot \frac{8}{\alpha l(v_c + v_a)} \left[\frac{v_c}{A - 1} - \frac{v_a}{A + 1} + \frac{8\nu FC}{\eta \alpha^2} \cdot \frac{1}{A^2 - 1} \right] \tag{9}$$

Now the right-hand fraction, according to equation 27 (see reference 2), equals $\frac{\kappa_\omega}{\kappa}$, where κ_ω and κ are the surface conductivity (not related to unit area!) and the volume conductivity, respectively; it follows that

$$X_0 - X = X \cdot \frac{\kappa_\omega}{\kappa} \tag{10}$$

That the field strength in the capillary, X, has another value than that outside, X_0, is a consequence of the *membrane potential*, Π. The latter is equal to $(X - X_0)L$, where L is the length of the slit, hence

$$\Pi = -\frac{\kappa_\omega}{\kappa} \cdot XL \tag{11}$$

or, inserting the value of X from equation 10,

$$\Pi = -\frac{\kappa_\omega}{\kappa + \kappa_\omega} \cdot X_0 L \tag{12}$$

The direction of this membrane potential difference is such that the additional field is opposite to the impressed electric field for positive as well as for negative membranes; X is always lower than X_0.

After the switching-off of the external field the membrane potential will vanish with a very great velocity; we can calculate that ca. 10^{-6} or 10^{-7} second is sufficient to reduce it to 0.01 of the original magnitude. But during the current's flow a measurement of Π must be practicable and perhaps will not be more difficult than the measurement of the surface conductance. A determination of both Π and κ_ω on the same capillary system would make it possible to verify the relation 12.

If the expression $X_0 - X$ from equation 9 is put into equation 6 or 7 we find the decrease of the salt amount before the slit, this decrease per second, ΔS, being equal to

$$\frac{1}{\nu F}(i_c^0 - i_c) = \frac{1}{\nu F}(i_a - i_a^0)$$

The equation thus obtained can, however, be very much simplified, if the slit is wide enough. Then the surface conductance is very small compared to the bulk conductance and we can put $X_0 - X = 0$; moreover all the other terms in the bracket of equation 6 or 7 will be negligible[3] except for the term $\frac{V}{hX}$. To the order of approximation of the Helmholtz theory, therefore,

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[3] A discussion of these terms will be found in the previous paper (reference 2).

$$\Delta S = -CV \tag{13}$$

The current $I = i_c^0 + i_a^0$ moves and decomposes $\frac{I}{\nu F}$ gram-equivalents per second. We may compare this amount to the loss of solute ΔS and we write the dimensionless relation

$$\frac{\nu F}{I} \cdot \Delta S = -\frac{CV}{ChlX_0(v_c + v_a)} = -\frac{u_0}{v_c + v_a} \tag{14}$$

where

$$u_0 = \frac{V}{hlX_0} = \frac{D\zeta}{4\pi\eta} \tag{15}$$

is the velocity of the electroösmotic flow in unit field, according to Helmholtz.

At the other side of the slit we have evidently a *gain* of the salt of the same magnitude ΔS.

Both the relations 12 and 13 are, as far as I can see, independent of the particular distribution of the electric charge across the electric double layer.

The value Π is one of the second order of magnitude like the surface conductivity, but ΔS is one of the first order like the electric endosmose, the stream potential, etc. Thus the concentration change at diaphragms was discovered at the same time as the laws of electroösmotic phenomena. Its extensive exploration has, however, been hardly undertaken.

Particularly A. Bethe and Th. Toropoff (1) have investigated the connection between ΔS and the electroösmotic behavior (at diaphragms of chromated gelatin chiefly).

The most important results of their experiments are as follows: (1) If in a 0.01N solution of sodium chloride we gradually replace the sodium chloride by hydrochloric acid, both the transported liquid volume V and the transported electrolyte amount ΔS change their magnitude and even their direction, but an approximate proportionality between ΔS and V subsists always (see figure 3 of the paper of Bethe and Toropoff). It seems to be a verification of our equation 13, since this can be applied also to a mixture of binary electrolytes of the same valence; C will be in this case the total concentration (in Bethe and Toropoff's experiments = 0.01N). Unfortunately the flow V is given by Bethe and Toropoff in conventional units only, so that it is not possible to show that the proportionality factor $\Delta S : V$ is really equal to C.

(2) In a $0.01N$ sodium chloride solution 1 coulomb has transported nearly 1.6×10^{-6} moles of sodium chloride to the cathode side of the diaphragm. Since 1 coulomb corresponds to 10^{-5} moles nearly, we obtain

$$\frac{\nu F}{I} \cdot \Delta S = \frac{1.6 \times 10^{-6}}{10^{-5}}$$

hence, according to equation 14,

$$-u_0 = 0.16\,(v_c + v_a)$$

The mobilities of Na^+ and Cl^- being 4.8×10^{-4} and 7.2×10^{-4} cm. per second per volt per centimeter, respectively (at 20°C.), we find $u_0 = -1.9 \times 10^{-4}$ and, according to equation 15, $\zeta = -0.027$ volt, a probable figure for the system $0.01N$ sodium chloride–chromated gelatin.

In a $0.01N$ hydrochloric acid solution 1 coulomb has transported nearly 1.5×10^{-6} moles of hydrogen chloride in the opposite direction; whence $\zeta = 0.087$ volt.

(3) Besides Bethe and Toropoff have observed and measured a "neutrality trouble," i.e., an appearance of alkaline reaction in the anode compartment and of acid reaction in the cathode compartment after the electroösmose in a $0.01N$ sodium chloride solution. But the "trouble" is so small (after the passage of 4 coulombs the pH has risen from 7.00 to 7.2–7.3 and fallen from 7.00 to 6.8–6.9, respectively) that it need not be taken into account.

SUMMARY

From the theory of the diffuse double layer expressions are derived for both the electrolyte transport and the potential differences at membranes through which an electroösmotic current is driven. These expressions are discussed and compared with the experimental evidence.

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ELECTROKINETIC PROPERTIES OF PROTEINS. III

THE RÔLE OF ELECTRICAL FORCES IN THE ADSORPTION OF GLIADIN AT A GLASS-LIQUID INTERFACE[1]

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INTRODUCTION

Streaming potential data presented in the preceding paper (13) of this series indicated that the rate of adsorption of gliadin at a glass-liquid interface was determined primarily by the sign and the magnitude of the electric charge of the protein micelles in relation to that of the glass, adsorption apparently being a mutual precipitation of the oppositely charged bodies. The rôle of electrical forces of attraction and repulsion in adsorption, and the reversibility of the process have been further investigated in the present work.

EXPERIMENTAL

Apparatus

The apparatus used in the preceding investigation (13) was modified to facilitate changing from one solution to another without interrupting the streaming potential measurements. This was accomplished by connecting the streaming cell through a three-way stopcock to two solution reservoirs, each of which was equipped with a mechanical stirrer. The apparatus was otherwise identical with that described in the above paper, and therefore needs no further description.

Materials

The gliadin preparation described in the previous paper (13) was used in these studies. All solutions were prepared from chemically pure sodium hydroxide, acetic acid, and conductivity water. The gliadin was dispersed in a 70 per cent ethanol solution and sufficient of the resulting sol added to the aqueous solutions to give a concentration of 0.002 g. of gliadin per liter.

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[1] Paper no. 43, Journal Series, from the Agricultural Experiment Station, Montana State College, Bozeman, Montana.

Calculation of the electric moment of the double layer at the solid–liquid interface

The values for the electric moment of the double layer at the solid–liquid interface were calculated from the streaming potential data by the formula of Bull and Gortner (6)

$$qd = \frac{\eta \kappa_s H}{P}$$

in which the C.G.S. constants are evaluated, as previously explained (13), to give

$$qd = 224755.22 \times \eta \times \frac{\kappa_s H}{P}$$

where q is the charge per unit area of the double layer in electrostatic units, d the thickness of the double layer in centimeters, η the viscosity of the streaming liquid in poises, κ_s the electrical conductance across the diaphragm in reciprocal ohms, H the streaming potential in volts and P the hydrostatic pressure in centimeters of mercury. The values for κ_s, H, and P were determined experimentally, and the values for η, the viscosity of the solutions, were assumed to be the same as that of water (9) at the temperatures at which the streaming potential measurements were made. Although the viscosity of aqueous solutions varies with composition and concentration, as shown by the work of Jones and Talley (10), the differences in the extremely dilute solutions used in these studies were not sufficient to be measured by the usual methods. The viscosity values for pure water were therefore used in the calculations.

ADSORPTION OF GLIADIN ON GLASS AS INFLUENCED BY ELECTRICAL FORCES OF ATTRACTION AND REPULSION

When a protein is dispersed in an aqueous solution it may ionize amphoterically to form electropositive, electroneutral, or electronegative micelles, the degree of ionization of its acidic or basic groups being influenced by the common-ion effect of the hydrogen and hydroxyl ions of the solution. Protein micelles are thus positively charged in acidic solutions, negatively charged in alkaline, and electrically neutral in isoelectric solutions. Glass, however, is electronegative in both acidic and alkaline solutions. It follows, therefore, that in an alkaline solution both the protein micelles and the glass are negatively charged, and consequently are repelled from each other. If, however, the hydrogen-ion concentration of the solution is progressively increased by adding increments of acid, the charge of the protein micelles will reverse when the isoelectric point is passed, and they will be precipitated on to the glass by the forces of attraction between the electric charges of opposite sign. The system will thus change from a glass–liquid to a glass–protein–liquid system, resulting in a reversal of the potential across the interface.

The foregoing was demonstrated experimentally by streaming a dilute sodium hydroxide solution containing 0.002 g. of gliadin per liter through the fritted glass diaphragm and measuring simultaneously the change in the streaming potential as the hydrogen-ion concentration of the solution was progressively increased by adding increments of dilute acetic acid.

The potential across the diaphragm quickly attained a constant value following addition of acid until it reversed in sign, after which it decreased gradually with time. All measurements were therefore made exactly 10 minutes after adding each increment of acid in order to obtain comparable results. Although the applied hydrostatic pressure was automatically maintained constant, the effective hydrostatic pressure decreased slightly during the progress of the measurements, owing to a lowering of the solution in the reservoir. Since the streaming potential is directly proportional to the hydrostatic pressure, the values for the ratio $H:P$, given in table 1, and represented by the curve in figure 1, show the influence of the hydrogen-ion concentration on the streaming potential.

TABLE 1

Effect of hydrogen-ion concentration on the adsorption of gliadin at a glass–liquid interface

HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	H/P	ELECTRIC MOMENT OF DOUBLE LAYER μ
pH	$\kappa_s \times 10^{-6}$	*cm.*Hg	*millivolts*		*e.s.u.* $\times 10^{-4}$
9.98	30.24	12.5	−279	−22.32	−13.35
9.79	25.26	12.3	−322	−26.18	−13.08
9.56	20.61	12.3	−390	−31.71	−12.92
9.07	16.98	12.2	−434	−35.57	−11.95
8.36	14.19	12.2	−469	−38.44	−10.79
7.41	12.22	12.1	−494	−40.83	−9.87
6.89	11.48	12.1	−501	−41.40	−9.40
6.29	11.02	12.0	+11	+0.92	+0.20
6.01	10.84	11.9	+53	+4.45	+0.95
5.55	11.14	11.9	+172	+14.45	+3.18
5.32	12.52	11.8	+185	+15.68	+3.88
5.10	14.19	11.6	+213	+18.36	+5.15
4.80	16.71	11.4	+223	+19.56	+6.46
4.48	23.95	11.2	+182	+16.25	+7.70

Viscosity of above solutions, η, is 0.0088.

To determine whether the gliadin was adsorbed from an alkaline solution in which its charge was the same as that of the fritted glass diaphragm, the charge of the latter was determined before and after streaming through it

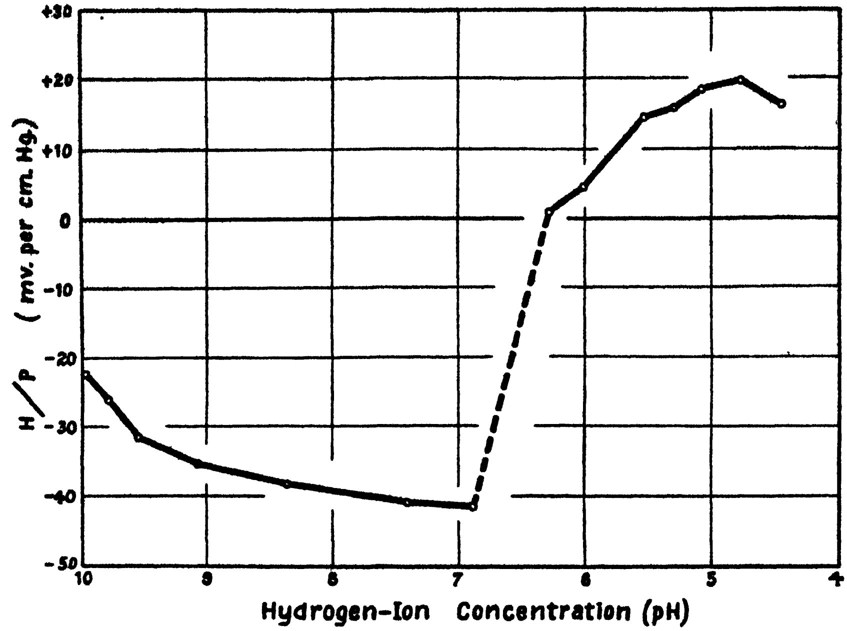

FIG. 1. THE REVERSAL OF THE STREAMING POTENTIAL BY THE ADSORPTION OF GLIADIN

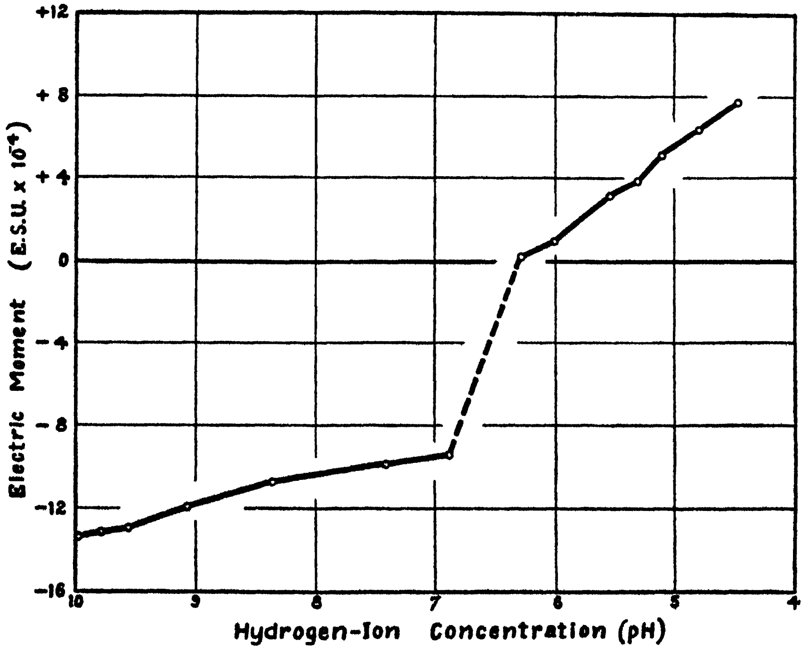

FIG. 2. THE REVERSAL OF THE ELECTRIC MOMENT OF THE DOUBLE LAYER AT THE GLASS-LIQUID INTERFACE BY THE ADSORPTION OF GLIADIN

TABLE 2

Adsorption of gliadin on glass in alkaline and acidic solutions

TIME	HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Acetic acid solution					
minutes	pH	$\kappa_s \times 10^{-6}$	*cm.*Hg	*millivolts*	*e.s.u.* $\times 10^{-4}$
0	4.46	15.44	11.8	−451	−12.86
5	4.46	15.44	11.7	−448	−12.89
10	4.46	15.44	11.6	−443	−12.85
Changed to sodium hydroxide solution					
12	10.10	29.12	11.7	−201	−10.91
15	10.10	29.12	11.7	−194	−10.53
20	10.10	29.12	11.6	−189	−10.34
25	10.10	29.12	11.6	−187	−10.23
30	10.10	29.12	11.5	−184	−10.18
0.002 g. gliadin per liter added					
32	9.80	30.65	11.6	−154	−8.87
35	9.80	30.65	11.6	−146	−8.41
40	9.80	30.65	11.5	−141	−8.19
45	9.80	30.65	11.5	−138	−8.02
50	9.80	30.65	11.4	−136	−7.97
55	9.80	30.65	11.3	−134	−7.92
60	9.80	30.65	11.2	−131	−7.82
Changed to sodium hydroxide solution					
62	10 08	28.91	11.9	−162	−8.58
65	10.08	28.91	11.8	−171	−9.13
70	10.08	28.91	11.8	−175	−9.35
75	10.08	28.91	11.7	−177	−9.53
80	10.08	28.91	11.7	−178	−9.59
85	10.08	28.91	11.6	−178	−9.67
90	10.08	28.91	11.5	−178	−9.75
Changed to acetic acid solution					
92	4.37	15.44	11.8	+13	+0.37
95	4.37	15.44	11.8	−6	−0.17
100	4.37	15.44	11.7	−14	−0.40
105	4.37	15.44	11.7	−15	−0.43
110	4.37	15.44	11.6	−16	−0.46
115	4.37	15.44	11.6	−18	−0.52
120	4.37	15.44	11.5	−19	−0.56
0.002 g. gliadin per liter added					
121	4.83	16.18	11.5	+72	+2.21
122	4.83	16.18	11.5	+105	+3.22
125	4.83	16.18	11.4	+134	+4.15
130	4.83	16.18	11.4	+149	+4.61
135	4.83	16.18	11.3	+154	+4.81
140	4.83	16.18	11.2	+159	+5.01
150	4.83	16.18	11.2	+166	+5.23
160	4.83	16.18	11.1	+169	+5.37

Viscosity of above solutions, η, is 0.0097.

an alkaline solution of the gliadin. The data from these measurements are presented in table 2 and figure 3. The charge of the diaphragm in an acetic acid solution of pH 4.46 and in a sodium hydroxide solution of pH 10.10 is shown by curves *AB* and *BC*, respectively, in the figure. At *C* 2 mg. of gliadin per liter was added to the alkaline solution and the resulting sol streamed through the fritted glass diaphragm for 30 minutes. The alkaline sol was then displaced from the diaphragm at *D* by a protein-free sodium hydroxide solution, which was streamed through the system for 30 minutes to remove any unadsorbed protein. Following this treatment the diaphragm was tested for adsorbed protein by determining the sign of its charge in a protein-free acid solution. As shown by curve *EF*, its charge reversed momentarily and then attained a constant negative value, which indicated that the surface of the glass had not been completely

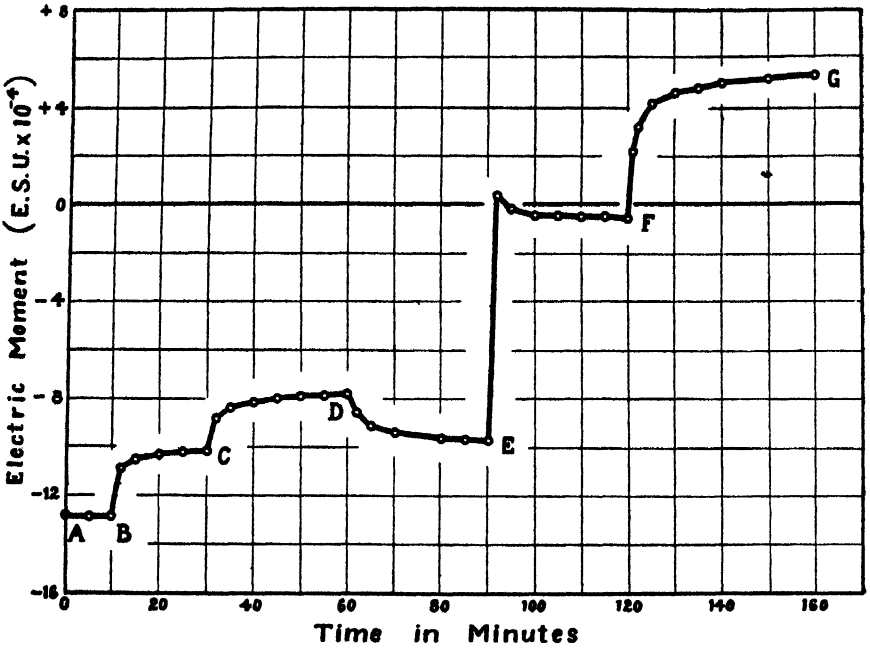

FIG. 3. STUDIES ON THE ADSORPTION OF NEGATIVELY CHARGED GLIADIN ON GLASS

AB, electric charge of fritted glass diaphragm in a protein-free acetic acid solution of pH 4.46.
B, changed to protein-free sodium hydroxide solution of pH 10.10.
C, added 0.002 g. gliadin per liter of streaming solution.
D, changed to protein-free sodium hydroxide solution of pH 10.08.
E, changed to protein-free acetic acid solution of pH 4.37.
F, added 0.002 g. gliadin per liter of streaming solution.
FG, electric charge of diaphragm in gliadin sol of pH 4.83.

TABLE 3

Effect of hydrogen-ion concentration on the desorption of gliadin from a glass–liquid interface

TIME	HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Dilute acetic acid solution					
minutes	pH	$\kappa_s \times 10^{-6}$	*cm.*Hg	*millivolts*	*e.s.u.* $\times 10^{-4}$
0	4.72	11.83	12.4	−314	−6.40
5	4.72	11.83	12.3	−312	−6.41
10	4.72	11.83	12.2	−309	−6.40
0.002 g. gliadin per liter added					
11	5.15	12.48	12.2	−187	−4.08
12	5.15	12.48	12.2	−66	−1.44
14	5.15	12.48	12.2	+50	+1.09
16	5.15	12.48	12.2	+91	+1.99
18	5.15	12.48	12.2	+112	+2.45
20	5.15	12.48	12.2	+124	+2.71
25	5.15	12.48	12.1	+137	+3.02
30	5.15	12.48	12.1	+142	+3.13
35	5.15	12.48	12.0	+145	+3.22
40	5.15	12.48	12.0	+147	+3.26
45	5.15	12.48	12.0	+148	+3.29
50	5.15	12.48	12.0	+147	+3.26
Changed to dilute sodium hydroxide solution					
51	8.37	13.76	12.6	−462	−10.77
52	8.37	13.76	12.6	−440	−10.26
54	8.37	13.76	12.5	−426	−10.01
56	8.37	13.76	12.5	−427	−10.04
58	8.37	13.76	12.4	−432	−10.24
60	8.37	13.76	12.4	−439	−10.40
65	8.37	13.76	12.3	−445	−10.63
70	8.37	13.76	12.3	−448	−10.70
75	8.37	13.76	12.2	−451	−10.86
80	8.37	13.76	12.2	−448	−10.79
90	8.37	13.76	12.1	−444	−10.78
100	8.37	13.76	12.0	−438	−10.72
Changed to dilute acetic acid solution					
101	4.72	11.69	12.0	+141	+2.93
102	4.72	11.69	12.0	+134	+2.79
104	4.72	11.69	12.0	+129	+2.68
106	4.72	11.69	12.0	+117	+2.43
108	4.72	11.69	12.0	+107	+2.22
110	4.72	11.69	12.0	+99	+2.06
115	4.72	11.69	11.9	+90	+1.89
120	4.72	11.69	11.9	+80	+1.68
125	4.72	11.69	11.8	+72	+1.52
130	4.72	11.69	11.8	+67	+1.42

Viscosity of above solutions, η, is 0.0095.

covered with the protein, otherwise it would have been positively charged in the acid solution. This was demonstrated by adding 0.002 g. of gliadin per liter to the streaming solution at *F*, which immediately reversed the charge of the glass as shown by the adsorption curve *FG*.

REVERSIBILITY OF THE ADSORPTION PROCESS

An attempt was made in the following experiments, the results of which are presented in table 3 and figure 4, to reverse the adsorption process by reversing the charge of the protein to the same sign as that of the glass on which it was adsorbed and thus to cause it to be desorbed by the electrical forces of repulsion.

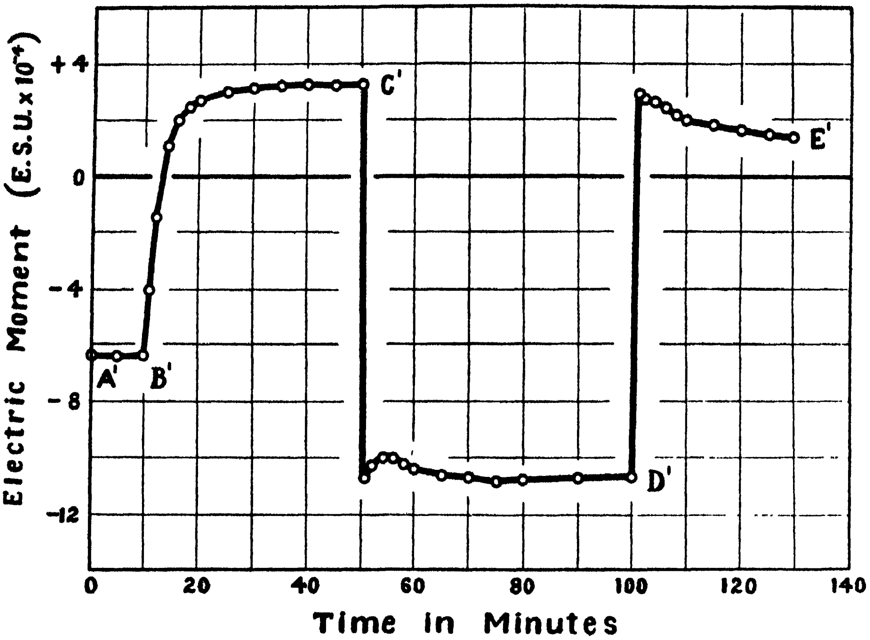

FIG. 4. IRREVERSIBILITY OF THE ADSORPTION PROCESS

A'B', electric charge of fritted glass diaphragm in a protein-free acetic acid solution of pH 4.72.

B', added 0.002 g. gliadin per liter of streaming solution.

C', changed to protein-free sodium hydroxide solution of pH 8.37. Solution was streamed through diaphragm for fifty minutes to remove any gliadin desorbed from the glass.

D', changed to protein-free acetic acid solution of pH 4.72.

D'E', electric charge of diaphragm in protein-free acetic acid solution of pH 4.72.

The charge of the protein-free diaphragm (glass) shown by curve *A'B'* in figure 4 was first determined by streaming through it an acetic acid solution of pH 4.72. At *B'* 2 mg. of gliadin per liter was added to the

TABLE 4

Influence of changes in hydrogen-ion concentration on the electrical properties of gliadin adsorbed at a glass–liquid interface

TIME	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Distilled water containing 0.002 g. gliadin per liter; κ_s = 1.44 × 10^{-6}; pH = 6.29			
minutes	*cm.* Hg	*millivolts*	*e.s.u.* × 10^{-4}
2	11.8	+1610	+4.42
4	11.8	+1609	+4.42
7	11.8	+1606	+4.41
12	11.7	+1598	+4.42
Sodium hydroxide added; κ_s = 1.48 × 10^{-6}; pH = 6.67			
2	12.6	−98	−0.26
4	12.6	−48	−0.13
6	12.6	−9	−0.02
8	12.5	+26	+0.07
10	12.5	+64	+0.17
12	12.5	+103	+0.27
14	12.5	+146	+0.39
16	12.4	+189	+0.51
18	12.4	+227	+0.61
20	12.4	+267	+0.72
22	12.4	+295	+0.79
Sodium hydroxide added; κ_s = 1.55 × 10^{-6}; pH = 7.10			
2	12.4	−1469	−4.13
4	12.4	−1408	−3.96
6	12.4	−1344	−3.78
8	12.4	−1278	−3.59
10	12.4	−1215	−3.42
12	12.4	−1164	−3.27
14	12.4	−1103	−3.10
16	12.4	−1049	−2.95
18	12.4	−1002	−2.82
20	12.3	−955	−2.71
22	12.3	−917	−2.60
Sodium hydroxide added; κ_s = 3.53 × 10^{-6}; pH = 8.07			
2	12.1	−1259	−8.26
4	12.1	−1245	−8.17
6	12.1	−1231	−8.08
Sodium hydroxide added; κ_s = 3.53 × 10^{-6}; pH = 8.07—*Cont'd*			
minutes	*cm.* Hg	*millivolts*	*e.s.u.* × 10^{-4}
8	12.1	−1220	−8.01
10	12.0	−1210	−8.01
12	12.0	−1202	−7.95
14	12.0	−1192	−7.89
16	12.0	−1181	−7.81
18	12.0	−1171	−7.75
20	12.0	−1161	−7.68
22	12.0	−1152	−7.62
Sodium hydroxide added; κ_s = 8.08 × 10^{-6}; pH = 8.83			
2	12.0	−583	−8.83
4	12.0	−583	−8.83
7	12.0	−582	−8.81
12	11.9	−574	−8.77
Sodium hydroxide solution containing 0.002 g. gliadin per liter; κ_s = 13.77 × 10^{-6}; pH = 9.49			
2	12.6	−414	−10.18
4	12.6	−413	−10.15
7	12.5	−412	−10.21
12	12.5	−411	−10.18
Acetic acid added; κ_s = 5.67 × 10^{-6}; pH = 8.45			
2	12.2	−496	−5.18
4	12.2	−503	−5.26
6	12.2	−522	−5.46
8	12.2	−532	−5.56
10	12.2	−540	−5.64
12	12.2	−549	−5.74
14	12.2	−557	−5.82
16	12.2	−562	−5.87
18	12.2	−569	−5.95
20	12.2	−572	−5.98
22	12.2	−574	−6.00

TABLE 4—*Concluded*

TIME	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Acetic acid added; $\kappa_s = 4.52 \times 10^{-6}$; pH = 7.41			
minutes	*cm.* Hg	*millivolts*	*e.s.u.* $\times 10^{-4}$
2	12.2	−273	−2.43
4	12.1	−281	−2.52
6	12.1	−294	−2.63
8	12.1	−303	−2.71
10	12.1	−308	−2.76
12	12.1	−311	−2.79
14	12.1	−315	−2.82
16	12.1	−318	−2.85
18	12.1	−320	−2.87
20	12.1	−322	−2.88
22	12.1	−324	−2.90
Acetic acid added; $\kappa_s = 4.63 \times 10^{-6}$; pH = 6.63			
2	12.0	0	0
4	11.9	−7	−0.06
6	11.9	−14	−0.12
8	11.9	−20	−0.17
10	11.9	−27	−0.24
12	11.9	−33	−0.29
14	11.9	−39	−0.34
16	11.9	−45	−0.39
18	11.9	−50	−0.44
20	11.9	−54	−0.47
22	11.9	−59	−0.52
Acetic acid added; $\kappa_s = 5.49 \times 10^{-6}$; pH = 5.38			
2	11.8	+363	+3.80
4	11.8	+356	+3.73
6	11.8	+347	+3.63
Acetic acid added; $\kappa_s = 5.49 \times 10^{-6}$; pH = 5.38—*Cont'd*			
minutes	*cm.* Hg	*millivolts*	*e.s.u.* $\times 10^{-4}$
8	11.8	+340	+3.56
10	11.8	+334	+3.50
12	11.8	+329	+3.44
14	11.8	+325	+3.40
16	11.7	+321	+3.39
18	11.7	+317	+3.35
20	11.7	+314	+3.31
22	11.7	+312	+3.29
Acetic acid added; $\kappa_s = 6.91 \times 10^{-6}$; pH = 4.88			
2	11.7	+438	+5.82
4	11.7	+433	+5.75
6	11.7	+430	+5.71
8	11.6	+428	+5.73
10	11.6	+427	+5.72
12	11.6	+425	+5.69
14	11.6	+424	+5.68
16	11.6	+422	+5.65
18	11.6	+421	+5.64
20	11.5	+419	+5.66
22	11.5	+418	+5.65
Acetic acid added; $\kappa_s = 10.39 \times 10^{-6}$; pH = 4.49			
2	11.5	+338	+6.87
4	11.4	+332	+6.81
7	11.3	+331	+6.85
12	11.2	+327	+6.82

Viscosity of above solutions, η, is 0.0100.

solution, which resulted in completely covering the glass with protein in 40 minutes, as indicated by the adsorption curve *B'C'*. The charge of the adsorbed protein was then reversed at *C'* by replacing the acid sol with a protein-free sodium hydroxide solution. The latter was streamed through the diaphragm for 50 minutes to remove any protein desorbed from the glass. Upon testing the diaphragm for adsorbed protein by again streaming through it a protein-free acetic acid solution of pH 4.72, it was found to be positively charged as shown by curve $D'E'$, which indicated that it was still covered with a layer of protein.

INFLUENCE OF CHANGES IN HYDROGEN-ION CONCENTRATION ON THE ADSORPTION EQUILIBRIUM AT THE GLASS–LIQUID INTERFACE

In measuring the charge of proteins adsorbed on porous diaphragms by the streaming potential method, it was observed in this and in the preceding investigations (12, 13) that the streaming potential did not attain a constant value immediately following the addition of acid or alkali to the solution streamed through the diaphragm, but that the potential increased positively following the addition of alkali and negatively following the addition of acid.

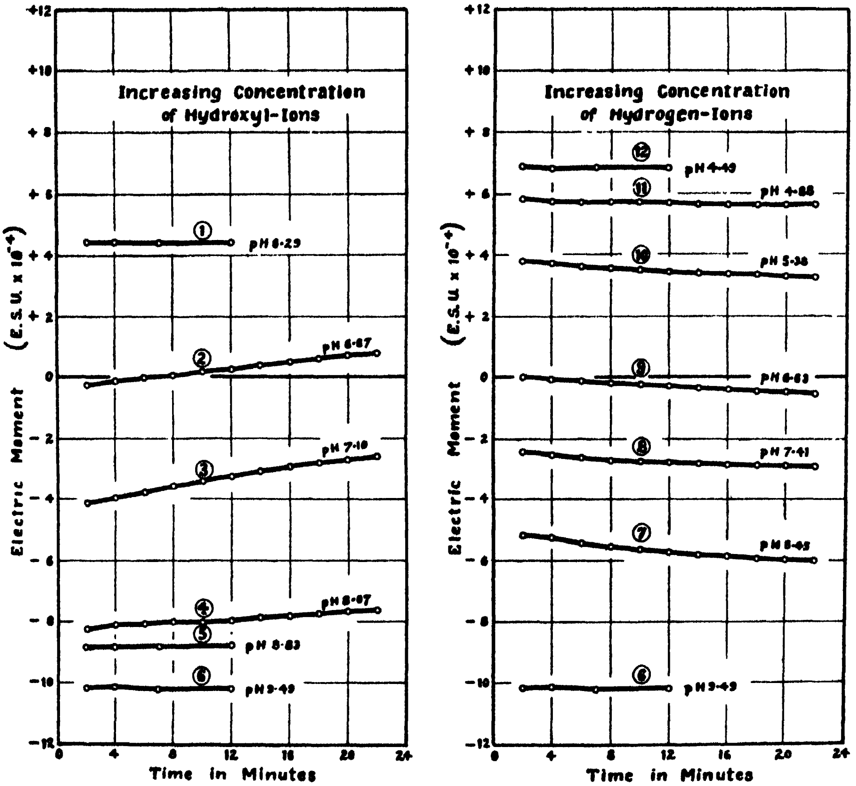

FIG. 5. INFLUENCE OF CHANGES IN HYDROGEN-ION CONCENTRATION ON THE ADSORPTION EQUILIBRIUM AT THE GLASS–LIQUID INTERFACE

Curve 1 represents the charge of the fritted glass diaphragm in equilibrium with distilled water containing 0.002 g. of gliadin per liter. Curves 2 to 6, inclusive, show the changes in the charge following successive additions of sodium hydroxide to the streaming solution, and curves 6 to 12 show the changes following the addition of acetic acid.

This effect is shown by the data in table 4 and by the electric moment–time curves in figure 5. Curve 1 in the figure shows the charge of the diaphragm which had come to equilibrium in conductivity water containing 0.002 g. of gliadin per liter; curves 2, 3, and 4 show the change in the charge following successive additions of sodium hydroxide to the solution. The charge of the diaphragm increased positively following each increase in the concentration of hydroxyl ions up to pH 8.83, after which equilibrium was quickly attained as indicated by curves 5 and 6. Upon reversing the foregoing procedure, however, by adding successive increments of acid to an alkaline sol, the charge of the diaphragm increased negatively following each addition of acid until the hydrogen-ion concentration reached pH 4.88, after which it became constant, as shown by curves 7 to 10 inclusive.

DISCUSSION

The streaming potential curve in figure 1 indicates that the fritted glass diaphragm adsorbed gliadin only from solutions in which its charge was opposite in sign to that of the glass. The abrupt reversal of the potential between pH 6.89 and pH 6.29, shown by the break in the curve, thus represents the transition from a glass–liquid to a glass–protein–liquid system, the change in potential being caused by the precipitation of the positively charged protein on the negatively charged glass. Although the streaming potential increased with increasing hydrogen-ion concentration from pH 9.98 up to the isoelectric region, the electric moment of the double layer at the solid–liquid interface decreased as shown by the curve in figure 2. This may have been due to the decrease in the total ionic concentration of the liquid phase, similar to that observed in the previous investigation (13), or it may have been caused by the adsorption of a positively charged protein fraction from the alkaline solution. The decrease in the charge of the diaphragm from that represented by curve *AB* to that of *EF* in figure 3 indicates that at least a trace of protein was adsorbed from the alkaline sol during the interval *CD*. The reversal of the potential following the addition of gliadin to the acetic acid solution at *F* indicates, however, that the glass had not adsorbed a complete covering of protein from the alkaline solution.

The curves in figure 4 show that the reversal of the charge of the protein to the same sign as that of the glass on which it was adsorbed did not result in its desorption. This is shown by the fact that the diaphragm was still positively charged in an acid solution after streaming through it for 50 minutes a protein-free alkaline solution. Obviously, if the protein had been desorbed from the glass it would have been removed by the liquid streamed through the diaphragm during the interval *C′D′*, and the potential across the interface would have been the same at *E′* as at *B′*.

When the drift or change in potential shown by the data in table 4 and by the electric moment–time curves in figure 5 was first observed in the earlier investigations (11, 12), it appeared to be caused by a decrease in the size of the pores of the diaphragm due to the adsorption of protein on their walls, the change in potential apparently being caused by the "back-pressure" effect of the small capillaries, similar to that observed by Bull (5), Abramson (2), and White, Urban, and Krick (18). However, the change in the positive direction following the addition of alkali, and in the negative direction following the addition of acid, as shown by the slope of the curves, indicates that the effect was due to a change in the equilibrium of the forces acting across the solid–liquid interface rather than to "back-pressure." This effect may have been caused by a disturbance of the adsorption equilibrium or by a change in the polarity of the adsorbed protein molecules through chemical reaction with the acid or alkali added to the streaming solutions. Abramson (3) has presented experimental evidence showing that proteins are adsorbed at a solid–liquid interface with the non-polar part of the molecule toward the solid phase and the polar groups toward the liquid phase. Daniel (7) has likewise shown that gelatin is adsorbed on quartz particles with the active groups oriented toward the liquid phase. It follows, therefore, that the change in potential represented by curves 2, 3, and 4 in figure 5 may have been caused by the reaction of the carboxyl groups of the adsorbed protein with the alkali added to the streaming solution, and that represented by curves 7, 8, 9, and 10 by the reaction of the amino groups with the acid, the rate of reaction being determined by the rate at which the acid or alkali ions were brought in contact with the adsorbed layer of protein by the solution streamed through the diaphragm. Curves 1, 5, 6, 11, and 12, however, show that a constant potential was quickly attained following the addition of acid or alkali to solutions more alkaline than pH 8.83 or more acidic than pH 4.88. This apparently indicates that all of the free amino and carboxyl groups of the adsorbed protein had combined with the acid and alkali, respectively, within the hydrogen-ion range pH 4.88 to pH 8.83. The change in potential across the solid–liquid interface observed in these studies may therefore have been caused, not only by an interchange between the proteins of the adsorbed layer and those dispersed in the liquid phase, but also by a change in the polarity of the adsorbed proteins due to salt formation.

It is evident from the data presented that the adsorption of gliadin on glass is an electrical precipitation process. The mechanism of adsorption of gliadin on glass is thus similar to that observed by Weinland and France (17), whose experiments showed that the adsorption of dyes by a growing crystal of sodium nitrate is dependent on the residual valency force fields of the crystal face, and on the distribution of the polar groups of the adsorbed dye molecules. That the mechanism of adsorption is the same for matter-in-mass as for molecules or micelles in the ionic state is indicated by the experiments of Northrop (14), which showed that the charge of glass was reversed by the adsorption of a layer of bacteria on its surface. Moreover, these data, as well as the observations reported in the previous paper (13), indicate that proteins prepared by the usual empirical methods are composed of two or more species of molecules having different isoelectric points, and that within the hydrogen-ion limits of the latter, part of the molecules are positively charged and part negatively charged, the proportion of each being determined by the common-ion effect of the hydrogen and hydroxyl ions. This accounts for the fact that protein preparations generally show an isoelectric *range* and not an isoelectric *point*, the latter usually being an interpolated value and not an experimentally determined point. It follows therefore that within the isoelectric range, the oppositely charged protein ions aggregate to form micelles, whereas outside this range their charges are of the same sign, and in consequence they are dispersed by the electrical forces of repulsion. The *true* isoelectric range thus appears to be the same as the "pH stability region" observed by Svedberg (16) and his coworkers.

The foregoing hypothesis not only accounts for the fact that the proteins show an isoelectric range rather than an isoelectric point, but it also explains why the experimental studies of a number of investigators, notably Abramson (1), Briggs (4), Daniel (7), Hitchcock (8), Loeb (11), Palmer (15), and Wintersteiner and Abramson (19), led to the general assumption that the adsorption of proteins on such inert substances as quartz, glass, and collodion was independent of the sign of the electric charge of the adsorbent and adsorbate. For example, the data of Hitchcock and Palmer show that collodion, which is negatively charged in dilute aqueous solutions, adsorbed a maximum amount of protein in the region of its isoelectric point, while those of Wintersteiner and Abramson show that quartz, which is likewise negatively charged in aqueous solutions, adsorbed insulin as readily from solutions on the alkaline side of its isoelectric point as from solutions on the acidic side. Granting that within the isoelectric range (pH stability region) the micelles are composed of both positively and negatively charged protein ions, it follows that the negatively charged adsorbents would selectively adsorb the positively charged protein ions from the micelles. Moreover, the magnitude of the charge of the individual protein ions associated as micelles would be lower in the isoelectric region and in consequence more of them would be required to neutralize the charge of the adsorbent. This explains why a maximum amount of protein is adsorbed in the isoelectric region.

SUMMARY

The rôle of electrical forces of attraction and repulsion in the adsorption of gliadin on glass has been studied by the streaming potential method. The results obtained support the following conclusions.

1. The adsorption of gliadin on glass from dilute aqueous solutions is an electrical precipitation process.
2. The adsorption process is not completely reversible.
3. A highly purified gliadin preparation is not chemically homogeneous, but contains within the isoelectric range both positively and negatively charged fractions.
4. Gliadin is adsorbed on glass with its free amino and carboxyl groups toward the liquid phase.
5. The free amino and carboxyl groups of the adsorbed gliadin react with acids and alkalis, respectively, within the hydrogen-ion range pH 4.88 to pH 8.83.
6. The *true* isoelectric range of a protein is probably identical with the "pH stability region."

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SUPERHEATING AND FOAMING PHENOMENA IN DEHYDRATING EMULSIFIED OILS[1]

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Crude petroleum oil, whether obtained from a level of a few hundred feet in the earth's crust or from a level of more than nine thousand feet, usually contains water. When oil and water pass through pipes to the earth's surface, or when pressure is released, an emulsion forms. As a matter of fact, over 200,000,000 barrels (42 gallons each) of emulsified crude oil are dehydrated yearly by means of heat, heat and pressure, chemicals, electrical energy, or combinations thereof.

Crude oil emulsions are usually of the water-in-oil type, while a few show the oil dispersed in water. Some manifest a double type emulsion of water-in-oil and oil-in-water, while others are of the water-in-oil type with oil also dispersed in the water drop. The water content of emulsified crude oils may vary from 0 per cent to over 90 per cent as produced. Emulsified crude oils are, in general, of a highly complex character; this study is directed toward their superheating and foaming characteristics.

The dehydration of emulsified oil by heat is based primarily upon lowering the viscosity and surface tension and changing the colloidal properties of the emulsifier. It is difficult to generalize on the specific effect of heat in the sense of changing the properties of the emulsifier, because the effect produced depends more upon the individual case to be treated, i.e., the nature of the components involved and the physical conditions of the system. A suitable increase in temperature is combined with a change in the state of aggregation, and the steam and oil vapor formed cause breaks in the surrounding protective films. Heat does not effect the separation of water and oil directly, but rather accelerates it. The accelerated precipitation of water does not occur solely on account of the increase in the difference in the specific gravity of the components due to heating. A more rapid precipitation of water on heating may be attributed rather to a decrease in the viscosity of the oil. The temperature to which an emulsion must be heated for complete dehydration depends to a certain extent upon the nature of the crude oil emulsion and may vary widely. When the temperature is increased, the density of the hydrocarbon oils decreases more rapidly than the density of water. In heating an oil from 15.55–65.5°C., the decrease in density amounts to about 7 per cent, whereas in heating water from 15.55–65.5°C., the decrease in density amounts to 1.1 per cent. For this reason it is possible to obtain a more rapid separation of oil and water at higher temperatures than at lower temperatures. At a given temperature and with oils of equal specific gravity, the one having the lower viscosity will separate more readily from water. This effect is pronounced when the amount of oil is large as compared with the amount of water. Increasing the temperature of an emulsified oil from 15.55–65.5°C. reduces its viscosity at times as much as 55 per cent. The rate of separation varies with the amount of material charged to the still, the size of the still, the amount and degree of dispersion of the water present in the oil, and the stage of the process.

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Two phenomena, well known to the industrial chemist, accompany heat dehydration: first, a priming or puking of the oil to be dehydrated, a kind of explosion caused by a superheating effect; second, foaming of the emulsion. Observations reveal that there is a certain relationship between these two phenomena. Some form of heat treatment is generally used for the removal of water from oil emulsions, therefore it is of interest to discuss both these phenomena.

If an emulsified oil is heated too rapidly, it usually causes the still to puke. Sometimes puking of the oil is effected by irregularities occurring in heating. Occasionally, when the same amount of the same oil is charged to three stills of the same size, one pukes more readily than the others.

Marcet (14) was the first to note that the temperature at which water and certain other liquids begin to boil varies with the nature and the state of the surface of the container in which the boiling takes place. These differences were attributed to a molecular change produced by the surface of the container, or by the presence of certain substances. It has been suggested that the part these substances play is to produce a more or a less perfect contact, or a more or a less close adhesion between the molecules of the liquid and the walls of the container. Whether the conversion of the liquid into vapor is made more difficult or, on the contrary, facilitated, is determined by the action of these substances.

Evaporation and ebullition are both molecular phenomena. Both, depending upon the action of heat, differ in the degree of vapor tension produced, as well as in the rapidity with which the change of the liquid into a vapor takes place. While in ebullition the change of the phase is sudden and visible, occurring simultaneously throughout the liquid, the change of the phase in evaporation is slow and always progressive, restricted to conversion into molecular vapor situated at the surface, or very close to it. Any factor increasing the cohesion of the molecules to each other, or their adhesion to the walls of the container in which they are enclosed, would have a tendency to slow down the evaporation of this liquid or delay its ebullition.

Donny (4), Dufour (5), and Faraday (6) found that water freed from air does not boil until it reaches a temperature of 132°C. and then it explodes. Water raised to a temperature of 132°C. under ordinary atmospheric pressure remains as water, but the introduction of the smallest amount of air or steam induces it to vaporize immediately and, at the same time, its temperature decreases. Donny assumed that the superheating phenomenon was due to a rupture either in the cohesion of the heated liquid, or in its adhesion to the container. Under ordinary conditions, liquids begin to boil approximately at a temperature required by their vapors so as to establish equilibrium with atmospheric pressure. By the effect of ebullition, liquids lose the greater part of the air held in solution, the boiling of the liquid being influenced principally by cohesion and adhesion. The liquid, free from air and heated beyond its boiling point, finally releases vapor explosively when a lowering of the temperature brings back a momentary quietness to the liquid. Cohesion is the force preventing, or at least delaying considerably, ebullition of liquids free from air. The phenomenon of priming or puking once started continues to reproduce the effect with an increasing violence. If the principle that the liquid has to be freed from air in order to produce the above phenomenon holds true then, by passing a gas through a liquid, the disturbing phenomenon may be avoided. Donny's experiments revealed that this holds true only for certain cases. De la Rive (3) and Dufour (5) studied the change of phases under the influence of temperature. They pointed out that the presence of a foreign substance in a liquid may hasten the evaporation, assuming that the change in phase does not necessarily occur when by heating the liquid a tension equal to the outside pressure is produced, but it may occur partially, owing to certain molecular conditions of the contact to which the liquid is subjected.

The molecular influences of contacts tend to promote vaporization at a minimum temperature. Owing to this fact, noticeable differences in boiling point are observed when water, alcohol, or sulfuric acid is heated in a glass or in a porcelain container (experiments by Donny (4), Marcet (14), and Magnus (12)), or when they are heated away from contact with solid particles. In some cases it appears that the contact of solid particles is a determining cause of the change of phase for fluids. If a globule of liquid comes in contact with a solid particle entrained by currents induced by heat, or with the walls of the container, a sudden production of a vapor bubble takes place. If water is mixed with sand (3) with a liquid layer of a few millimeters thickness, the water evaporates more rapidly in air than the same quantity of water alone. Thus the temperature of a water–sand mixture evaporating in air is lower than that of water exposed alone under the same conditions. Water containing sea salt also evaporates less rapidly, producing a smaller degree of cooling by its evaporation than water under the same conditions.

Kenrick (10) and his coworkers studied the superheating phenomenon of liquids. A study was made of the extent to which liquids may be superheated and the physical conditions under which superheating is possible, i.e., where temperatures are equal to or higher than those where the elastic force of the liquid produces equilibrium to the external pressure. The question regarding the location of the ebullating and superheating influences also appeared of interest to these investigators. They assumed that ebullition takes place locally, either at a few fixed points on the walls of the vessel, or from particles suspended in the liquid from which actually streams of bubbles rise. If this be true, then the superheating effect should depend on the ability of the liquid to wet the material which serves as a nucleus.

TABLE 1

Association coefficient of liquids as determined by Gilbert

LIQUID	HIGHEST TEMPERATURE	PRESSURE	BOILING POINT	ASSOCIATION COEFFICIENT
	degrees C.	*mm.*	*degrees C.*	
Ethyl ether	143	11,500	35	1.0
Ethyl alcohol	201	22,700	78	2.7
Methyl alcohol	180	20,100	63	3.4
Chloroform	173	11,000	61	1.0
Acetone	174	14,400	56	1.3
Carbon bisulfide	168	11,700	46	1.0
Water	270	41,200	100	2.3-3.8
Sulfur dioxide	50	6,300	−10	1.0
Benzene	203	11,200	79	1.0
Chlorobenzene	250	8,300	132	
Bromobenzene	261	6,100	156	
Aniline	262		183	
m-Xylene	235		137	

Kenrick found a gradation in the effectiveness of the nuclei present. Some of them caused ebullition when the liquid was slightly superheated; others were effective only when it was heated to a higher temperature. Experimentally, it was not clear whether there was a real temperature limit or merely a rapid shortening of the time interval with increase in temperature. He also found that the smaller the vessel in which the liquid is heated, the higher the temperature to which it could be heated without boiling. Wismer (19) calculated the diameter of a spherical particle acting as a nucleus enclosed by bubbles and found that it was equal to 5×10^{-7} cm. Calculation of the pressure in the bubbles gave a value of about 12.5 atmospheres, corresponding to a temperature of about 130°C. (extrapolated). Gilbert (7) calculated the amount of vapor in a bubble whose pressure, caused by surface tension, balances the outside vapor pressure. Quantities about one hundred times greater than those corresponding to the ordinarily accepted molecular dimensions were determined. This led Gilbert to the conclusion that liquids which can be heated to temperatures corresponding to abnormally high vapor pressures are those which are abnormal in possessing high association coefficients as shown in table 1.

Wismer (18) determined the pressure–volume relations for ether at 121°, 128°, and 134°C. and at corresponding pressures above 30 atmospheres to as low as 1 atmosphere. He made similar measurements with ethyl chloride at 99°, 110°, and 117°C. The P–V curve in both cases appeared to be almost a straight line, and showed no sign of more rapid curving as the limit of superheating was reached, although in both cases the temperatures reached at atmospheric pressure were above the maximum calculated from van der Waals equation.

The most characteristic points in the superheating effect are the extent to which superheating of a given liquid is carried out and the time during which a liquid is kept under these conditions. It was observed that these characteristics vary from one experiment to another. Kenrick, Gilbert, and Wismer (9) attempted to work out these questions concerning superheating phenomenon. Previous work (1, 20) indicated that the superheating of liquids is closely allied to the "stretching" phenomena of liquids (15), as well as to the supersaturation of gases (19).

Supersaturation is favored by long heating of a solution at high temperature. Liquids saturated with gases at concentrations corresponding to a pressure over 100 atmospheres showed that when the pressure was reduced to 1 atmosphere, no bubbles were formed in the liquid. In the case of superheating of liquids, Kenrick, Wismer, and Wyatt observed that with a rise in temperature there is a very rapid shortening of the time interval between the lowering of the pressure and the formation of bubbles, in spite of the fact that the adsorption coefficient of the gas decreased but little with rise in temperature. There is definite evidence in favor of the old theories on the superheating phenomenon, namely, that liquids must be free from gases and air in order to undergo superheating effects.

Krebs (11) removed air from water by mixing it with alcohol (about three times the volume of water) and boiling down the mixture to a small volume (the boiling point rose steadily to 107°C.). When a very large flask was used and the mixture evaporated to a small volume, the boiling point could be increased still more. In the boiling of this water–alcohol mixture, Krebs observed for the first time the coëxistence of superheating and foaming.

There is a certain analogy between the superheating phenomenon in liquids and in emulsion systems. But in the latter, the superheating effect finds its explanation rather in the behavior of the interfacial phase. As early as 1836, Magnus (13) showed that water with oil poured over it presents a considerably delayed ebullition. If oil is poured upon water, the explosive boiling is much more violent. Rideal (16) proved that evaporation of water from a surface is considerably diminished in the presence of fatty acids, such as stearic and oleic, as compared with evaporation from a free surface (8). An increase in the concentration, or in the pressure, upon the surface may also delay evaporation. It is to be expected that surface layers in a condensed or a vapor state primarily influence evaporation. When an oil-water emulsion is heated, the continuous phase, which is covered with a thin layer of oil, must be heated to a higher temperature, to start boiling, than that required to start the boiling of pure water. A sudden decrease from a higher boiling temperature to a lower may be attributed to a change in the Brownian movement during the heating, causing a cessation in the continuity in the interface oil skin and a decrease in temperature.

Taylor (17) in his article "The Structure and Decomposition of Liquid Skins" states that monomolecular layers actually have thick spots which interfere with their stability. It is possible that the problem of whether skins in the interface play a part in the explanation of the superheating phenomenon in emulsion systems may be solved experimentally, using dyestuffs. Frumkin, in a work on spreading dye substances on a water surface, proved that a competition of two substances over the same water surface can be demonstrated. When a drop of oleic acid is placed on a water–crystal violet (dye) surface, then the oleic acid molecules displace the dyestuff molecules and the dyed layer sinks to the bottom in streams. On a water surface previously covered with an oleic acid film, the crystal violet particles of dye remain colorless upon the surface. Tetraiodofluorescein may be used similarly. Perhaps, by means of such a dyestuff, it will be possible to prove whether superheated water in an oil–water emulsion is actually covered with a thin layer of oil, causing a decrease in evaporation, depressing ebullition and, consequently, producing the superheating effect during dehydration of crude oil emulsions.

Foaming is a phenomenon intimately connected with heat dehydration of emulsified oils. Emulsions, in their original form, often cannot be subjected to distillation without high danger of foaming over. The foaming is, of course, undesirable, not only because distillation must be repeated, but also because of the ever-present danger of fire. A belief is entertained that incipient foam formation with a rapid breaking down of the foam may play a large part in the mechanism of dehydration itself. Pressure and high temperature are two factors which favor the dehydration process, reducing at the same time the foaming tendency of the emulsion system. Pressure weakens the foam film structure; at higher temperatures the ability of oil to make and to maintain individual foam laminae is decreased. In petroleum emulsions the emulsifying agent is usually asphalt, "soaps," or mineral matter, and the decreased foaming with increase in temperature is due less to change in composition at the temperature at which foaming ceases than to a decreased protective action.

A number of experiments were carried out in connection with foam formation in heat dehydration of emulsified crude oils. The first question arising in connection with the problem concerns itself with the conditions under which foam originates in crude oil emulsions.

1. It was found that for the same temperature more water may be separated from an emulsion where a vapor space is present, than where no vapor space exists.

When one-quarter, one-half, or three-quarters of the still capacity was charged with a crude oil emulsion having 36 per cent of water and heated to 121.1°C. under a pressure of 2.74 kg. per square centimeter, 10 to 12 per cent of water was separated. When a full charge was maintained at the same temperature, 121.1°C., although using a pressure of 3.31 kg. per square centimeter only 6 per cent of water separated out.

The lack of vapor space prevents substantial foam formation which, in all probability, accounts for the difference in the dehydration effect.

2. A series of tests was made with sixteen samples of California emulsified oils to determine their foaming properties. The emulsified oils to be investigated were charged in beakers, immersed in a glycerol heating bath, and the foaming properties and height of the foam noted. The California emulsified oils which were experimented with had a water content ranging from 6 per cent to 69 per cent. The temperature of the glycerol bath in these comparative tests was maintained constant at 177°C. It was found that under the temperature conditions prevailing the foam column in the emulsified crude oil varied from 1½ in. to over 5 in. in height. It is interesting to note that a mixture of California oils No. N6 and N2 taken in equal portions showed a foam column height which was higher than when the oils were subjected singly to the same heating. California oil No. N6 with 6 per cent water: foam height, 3.8 cm. California oil No. N2 with 30 per cent water: foam height, 10.5 cm. A mixture of the two oils in equal proportions: foam height, 11.8 cm.

This brings out, as far as these tests are concerned, that the properties of emulsified crude oils as to foaming are not additive when mixed. One would expect that the foam column of California oil No. N2 would be reduced, owing to the addition of an oil having a low water content. However, this is not the case. As a matter of fact, the diluted oil No. N6 did not decrease the foam column, but actually increased it.

3. Distilling of crude oils of different origin revealed that foam formation in emulsified oils depends greatly upon the nature of the crude oil. The crude oils compared were derived from Casmalia, Santa Maria, Lompoc, and Efson oil wells. Casmalia oil is very persistent in foaming; Santa Maria oil foams slightly; Lompoc oil foams strongly; Efson oil foams, showing explosive characteristics.

Some emulsified oils distill quickly and then begin to foam after distillation has proceeded for a while, whereas other oils foam violently from the beginning of heat application.

Lompoc emulsified oil from Efson well No. N10 produced more foam at 149°C. than any Santa Maria crude oil tested, but Casmalia crude oil was the most persistent foam producer of all those experimented with. It was found further that the Lompoc oil acted in an explosive manner when heated. To overcome the violent bumping of this oil, gasoline was added to it and the foaming test conducted. The oil evaporated in a much less violent manner, but spattered and spat during the heating, and the foam was not persistent. This indicates that the gasoline added to the Lompoc emulsified oil has a marked influence upon its foaming and evaporating properties.

Some emulsified oils, upon application of heat, form relatively small foam bubbles, while others produce large bubbles.

4. The effect of temperature on the foaming properties of the emulsified oil was studied as a function of the depth of the liquid placed in the tubes. The oil investigated was Santa Maria crude oil containing 29 per cent of water. The procedure was to charge glass test tubes 2.24 cm. in diameter and 20.3 cm. long filled with 1, 2, and 3 cc. of Santa Maria emulsified oil which were immersed to 17.8 cm. of their length in a heated glycerol bath. After the glycerol bath reached the desired temperature, the tube containing the emulsified oil was placed therein. At the beginning of the test, the emulsified oil distilled quietly, with little foaming. As vapors passed from the top of the tube, a time was reached when the foam which started in a fine dispersion became coarse and persistent. The foam rising in the tube became at times somewhat irregular, seeming to give a breathing action, but finally attained a maximum and then gradually subsided. The maximum height which the foam column reached was recorded and all comparisons made in a similar manner.

It was found that the foam column of the Santa Maria emulsified oil increased as a function of the depth of the oil in the tube, and also increased as a function of the temperature employed, to a maximum which was attained at a glycerol bath temperature of 140°C., the foam column decreasing as the temperature of the bath reached 176°C.

Table 2 gives the order of the foam formation, as a function of the temperature variation, and depth of liquid employed during this set of experiments.

5. Finally, from a series of tests in which California emulsified crude oils were dehydrated, it was ascertained (a fact already indicated by Krebs (11), that foaming in heat dehydration was combined with the superheating effect discussed previously, as well as with self-cooling. Usually, during the heating of California emulsified oils, the temperature rose quite rapidly to a little above the boiling point of water, where it remained relatively constant for a time until a portion of the water was distilled from the oil, the temperature rising until a maximum was reached where the oil was dehydrated with a few fine drops of water still dispersed in the tar residue. With several of the emulsified crude oils, a marked departure from the behavior just described was noted.

TABLE 2

Order of foam formation

TEMPERATURE OF BATH	VOLUME OF EMULSIFIED OIL USED		
	1 cc.	2 cc.	3 cc.
degrees C.			
125	16	19	32
140	32	52	80
150	34	49	70
160	26	42	50
176	23	33	44

TABLE 3

Foam in heat dehydration combined with superheating effect and self-cooling

PHASES IN HEATING PROCESS	TEMPERATURE IN DEGREES C.	CHARACTERISTICS OF FOAMING
	Oil sample No. 1	
I Phase	Up to 111.1	Little foaming
II Phase	Drop in temperature to 102.2 constant for a time	Foam column rising
III Phase	Rise in temperature from 102.7 to 104.4	Foam column starting to collapse
	Oil Sample No. 2	
I Phase	Up to 107.2	Slight foaming
II Phase	From 107.2 to 102.2	Foaming increases
III Phase	From 101.6 to 111.1	Foaming rapidly recedes
	At 150.0	Foaming almost zero

Santa Maria crude oil from Rice Ranch well No. N2 showed a distinct superheating effect with rise in temperature followed by more or less foaming, a drop in the temperature of the oil taking place despite the fact that the oil was still being heated. In other words, water was apparently held in the oil above its boiling point, and by this superheating suddenly formed steam, with cooling taking place in the liquid. The mechanism would, therefore, be either that the oil system during this period absorbed heat from the oil faster than from an external source to an extent of producing a cooling effect (manifested by an actual drop in the temperature of the oil), or, under critical temperature conditions, the protective films were ruptured, or else chemical changes occurred in the emulsifying agent (a dissociation of the hydrates of the hydrocarbons present in the emulsified crude oil system), which took heat from the system, thereby cooling it.

In table 3 are illustrated (on two samples) the three phases in heat conditions of a Rice Ranch Santa Maria crude oil emulsion accompanied by foaming.

SUMMARY

Two phenomena accompany heat dehydration of emulsified oils: priming or puking, and foaming, resulting from superheating water.

Superheating of various liquids may be compared with superheating of emulsified oils. The conversion of a liquid into its vapor state is influenced by the character of the surface of the container in which the boiling occurs, or by the presence of solid particles in the liquid. Cohesion of molecules of the liquid or their adhesion to the walls of the container or suspended solids slows down evaporation and delays ebullition. Liquids freed from air are apparently a critical condition for the delay in ebullition. The extent of superheating is determined by the temperature necessary for sustaining equilibrium of the liquid against external pressure. Ebullition is restricted to certain localities in the liquid. A gradation in the effectiveness of the material serving as a nucleus for the superheating phenomenon is observed. The extent to which superheating of a liquid is carried out, and the time during which it is held under a superheated condition are the characteristics and the variables in the process.

An analogy between superheating and foaming effects in liquids and emulsions may be postulated, considering the significance of the interfacial phase in the case of emulsions. A thin layer of oil spread upon superheated water in an oil–water emulsion is responsible for the decrease in the evaporation of the system, depressing ebullition.

The mechanism of dehydration includes, in addition to the prevention of the superheating influences, the break-down of foam formed during the process. Pressure and high temperature favoring dehydration likewise reduce the tendency of the emulsion system to foam. At the same temperature, more water may be separated from an emulsion where a vapor space is present than where no vapor space exists. The lack of vapor space substantially prevents foam formation, thus accounting for changes in the dehydration effect. The properties of emulsified crude oils with respect to foaming are not additive. The intensity and persistence in foaming of emulsified oils which are to be dehydrated is decided by the nature of the oil. Foaming and evaporation of water from the emulsified oil are markedly influenced by certain substances, for example, gasoline. The foaming of emulsified oil increases as a function of the depth of the oil in the container, reaching its maximum at a definite temperature.

Superheating and foaming observed in the dehydration of emulsified oils produce evidence for the existence of a self-cooling effect. The latter may be interpreted as a result of superheating when the heat from the oil is adsorbed faster than from an external source. It may also be due to a rupture of protective films or else to chemical changes occurring in the system, requiring heat to be taken from the system itself and thereby cooling it.

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A SOURCE OF ERROR IN THERMOCHEMICAL MEASUREMENTS MAKING USE OF COMMERCIAL OXYGEN

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In a previous paper (1) it has been shown that the apparent value obtained for the water equivalent of a calorimeter is dependent not only upon the small amounts of combustible impurities usually present in commercial oxygen, but also upon the pressure in the cylinder at the time of delivery of its contents into the bomb. With the particular samples of oxygen (denoted G and K) by means of which this phenomenon was first brought to light, there was a gradual decrease in the apparent value for the water equivalent; this decrease ultimately reached seven and five parts per ten thousand for G and K, respectively, after the pressure in the cylinder had dropped from about 125 to 35 atmospheres. It will be the object of the present paper to investigate whether compressed oxygen does always show the same behavior under the particular conditions prevailing in bomb calorimetry.

I. THERMOCHEMICAL DATA IN SUPPORT OF THE CONTENTION THAT THE PURITY OF THE OXYGEN DELIVERED INTO A BOMB IS DEPENDENT UPON THE PRESSURE IN THE OXYGEN CYLINDER AT THE TIME OF DELIVERY

Two series of combustions were carried out with a constant amount of standard benzoic acid in the bomb and at a fixed initial temperature; for the first series, oxygen (sample J) from unknown origin was used throughout, while for the second series, the oxygen (sample M) had been obtained from liquid air by fractionation. In both cases the oxygen was delivered into the bomb to a constant pressure of 35 atmospheres.

A. Data relative to oxygen J

In order to estimate from the figures in table 1 the amounts of the combustible impurities present in the oxygen delivered at the various pressures, it is necessary to compare them with those obtained from the head portions of four different cylinders of oxygen, namely, L, K, G, and E (see table 2), by means of which the value of a constant heat capacity had been determined in an earlier series of combustions with the same preparation of standard benzoic acid and under exactly the same conditions as in the case of oxygen J (or later on oxygen M). In the case of oxygen E, all traces of combustible impurities had been removed by a previous purification.

It is difficult to suppose that such a remarkable agreement between so many individual values and especially between the means, which are identical for all practical purposes, is entirely due to chance. When it is further taken into account that there is a similar kind of agreement between the heats of combustion found at various periods with several different cylinders of oxygen, when the precaution was taken to determine the water equivalent with the same oxygen as for those heats of combustion and as simultaneously as possible with the latter, it must be concluded that the influence of chance must obviously be ruled out altogether.

TABLE 1

Apparent variation of the water equivalent for decreasing pressures of the oxygen in cylinder J

PRESSURE	WATER EQUIVALENT	MEAN WATER EQUIVALENT
atmospheres	*cal.*$_{15}$ *per degree*	*cal.*$_{15}$ *per degree*
122 ± 1	4274.7	4273.6
	4273.3	
	4272.8	
90 ± 1	4273.6	4273.6
71 ± 1	4275.5	4275.9
	4276.3	
38 ± 3	4275.4	4275.1
	4274.8	

B. Data relative to oxygen M

The results obtained for the apparent value of the water equivalent with some new oxygen (M) were found to be strikingly similar to those just recorded for oxygen J, as will appear from an examination of tables 3 and 4. The similarity is so complete, indeed, that the values obtained with sample J may be used for sample M as well for all pressures recorded, at least within the very small margin of a few tenths of 1 calorie for the experimental error.

In order to simplify the problem raised by the above data, it was felt advisable to arrange the experimental conditions so as to obtain results which could correspond only to one impurity at a time. Such a result was not impossible to attain by purely thermochemical means, namely, by preparing or purifying some oxygen and then adulterating it with a known amount of one single and well-defined impurity. But as it meant purifying compressed oxygen at a temperature of about 800°C. in order to free it from any combustible impurity possibly contained in it, or alternately purifying oxygen at ordinary pressure and afterwards compressing it to at least 100 atmospheres, it introduced considerable technical difficulties. Such a solution will be tried in the future, as soon as some conditions required for its successful fulfillment will have been realized. For the present a simpler, though quite efficient, procedure has been devised, which is based upon the fact that in the combustion inside the bomb, under well-defined conditions, of a constant amount of a definite substance in the presence of oxygen containing a small amount of nitrogen as impurity, a constant proportion of the latter is converted to nitric acid; by means of a simple titration of the acid with standard alkali the percentage of nitrogen impurity present in any one bomb filling may thus be determined.

TABLE 2

Values obtained for the water equivalent for pressures above 100 atmospheres in the cylinder and 35 atmospheres in the bomb, with oxygen from the cylinders L, K, G, and E

OXYGEN	PRESSURE IN CYLINDER	BENZOIC ACID USED NO.	WATER EQUIVALENT	MEAN WATER EQUIVALENT
			$cal._{15}$ per degree	*$cal._{15}$ per degree*
L	121/102	48a	4277.6 4276.9	4277.2
K	116/113	48a	4276.3 4276 5 4277.8 4277.4	4277.0
K	112/109	39b	4276.8 4277.0 4276 5 4278.7	4277.2
G	123/121	39b	4277.7 4277.0 4276 6	4277.1
E	Preheated	39c	4277.4 4278.0 4276.3 4275.6 4278.0	4277.1

II. PREPARATION AND ANALYSIS OF A MIXTURE OF OXYGEN AND NITROGEN IN SUITABLE PROPORTIONS AND UNDER A TOTAL PRESSURE OF ABOUT 100 ATMOSPHERES

A mixture of oxygen and nitrogen containing approximately 0.1 per cent of nitrogen was first prepared. This mixture was then used for combustions of a fixed amount of 1.72 g. of pure salicylic acid, under a constant pressure of 35 atmospheres in the bomb and with a calorimeter at a constant initial temperature of 20.5°C. The successive amounts of nitric acid found as the pressure in the cylinder decreased from 110 to 15 atmospheres have been collected in table 5. The results recorded for pressures in the cylinder which were lower than the final pressure in the bomb have been obtained by means of the following artifice: the bomb was first filled to a pressure of

TABLE 3

Apparent variation of the water equivalent for decreasing pressures of the oxygen in cylinder M

PRESSURE IN CYLINDER	WATER EQUIVALENT	MEAN WATER EQUIVALENT	MEAN ERROR FOR MEAN IN PARTS PER THOUSAND
atmospheres	*cal.₁₅ per degree*	*cal.₁₅ per degree*	
135/132	4273.3 4273.1 4275.2	4274.0	0.05
80/77	4275.6 4275.7 4275.6	4275.6	0.00
47/44	4274.2 4275.7 4275.5	4275.1	0.03

TABLE 4

Comparison between the variations in the water equivalent when determined with oxygen J and oxygen M, respectively

PRESSURE IN CYLINDER	MEAN WATER EQUIVALENT		NUMBER OF COMBUSTIONS
	Oxygen J	Oxygen M	
atmospheres	*cal.₁₅ per degree*	*cal.₁₅ per degree*	
135		4274.0	3
120	4273.6		3
80		4275.6	3
70	4275.9		3
40	4275.1	4275.1	3 + 3

15 atmospheres with the oxygen–nitrogen mixture; it was then connected with the particular cylinder of nitrogen-free oxygen already used for making up the oxygen–nitrogen mixture, until the pressure had risen to the usual mark of 35 atmospheres, in order to allow for the lesser amount of nitrogen impurity introduced in the bomb as the result of this procedure. Three blank combustions were also carried out with the nitrogen-free oxygen.

A consideration of table 5 shows that there is first an unmistakable increase in the amount of nitric acid formed during the successive combustions, as the pressure in the cylinder decreased from 110 to 55 atmospheres; indeed, for a pressure of 81 to 74 atmospheres, the amount of nitrogen converted to nitric acid was found to be just double of that obtained at the higher pressure; and for a further drop of pressure down to 61 to 55 atmospheres, the amount of nitric acid formed was four times as large as the original amount found. When, however, the pressure in the cylinder had fallen to about 20 atmospheres, the results obtained for the nitric acid were just below those found at the very start (after the difference between the mean for these results and the mean for the blanks had been multiplied by the factor 15/35 in order to allow for the lesser concentration of the nitrogen impurity in the three final bomb fillings made with the nitrogen mixture and thus to render the final data entirely comparable with the original ones).

TABLE 5

Mean correction to be applied to the water equivalent for different ranges of pressure in the cylinder in order to allow for the formation of nitric acid

PRESSURE IN CYLINDER	NITRIC ACID CORRECTION	MEAN NITRIC ACID CORRECTION
atmospheres	*calories*	*calories*
106/98	0.3 0.8 0.7	0.6
81/74	0.5 1.3 2.1	1.3
61/55	1.9 2.6 2.7	2.4
20/18	0.0 0.5 0.1	0.2

CONCLUSIONS

Whatever the true cause of the phenomenon recorded in the preceding pages, the following conclusions will apply:

(1) The statement made in a previous paper that the concentration of a combustible impurity eventually present in compressed oxygen may vary appreciably with the pressure in the cylinder at the time of delivery into the bomb, has been confirmed with three more cylinders of oxygen, one of unknown source and the other two derived from liquid air.

(2) The apparent value for the water equivalent of a calorimetric system, when determined by means of oxygen from any of these cylinders, all received from the British Oxygen Company, showed a total variation of the order of five to seven parts in ten thousand, which therefore cannot be ignored if a precision of the order of one or two parts per ten thousand is to be secured.

(3) The character of the curve, water equivalent against pressure in the cylinder, as revealed by the investigation of four different cylinders, may take one or other of two different forms, presumably depending upon the nature of the combustible impurity causing the contamination.

In conclusion, the author wishes to tender his thanks to Prof. E. C. C. Baly, Head of the Inorganic Department, for the facilities provided for this research.

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CHROMIUM HYDROXIDE HYDROSOLS AND THE BURTON-BISHOP RULE

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INTRODUCTION

Burton and Bishop (3), working with copper, gum mastic, and arsenious sulfide hydrosols, concluded that the flocculation values increase with decreasing concentration of sol for monovalent ions, remain about the same for divalent ions, and decrease for trivalent ions. This conclusion is referred to as the Burton-Bishop rule (4). It has been demonstrated that, whereas moderately purified ferric oxide and chromic oxide sols do not follow the above rule for monovalent ions (2, 5, 6), highly purified ferric oxide sols do (4). The experimental results presented in this paper show that highly purified chromic hydroxide hydrosols, like ferric oxide hydrosols, follow the Burton-Bishop rule.

PREPARATION OF SOLS

Normal ammonium hydroxide was slowly dropped into a normal chromium chloride solution at 60–70°C. with constant shaking until six-tenths of the stoichiometric amount had been added. Two purified sols were prepared from the stock sample by dialysis in collodion bags. Table 1 gives data on the preparation and some of the properties of the two sols.

RESULTS

Flocculation values were determined in the usual standard manner (4) and are reported as millimoles of electrolyte per liter of solution. With all sols flocculation values were determined with the original sol, referred to as 100 per cent, and concentrations of 80, 60, and 40 per cent of the original, dilution being made with water and, in some instances, with ethyl alcohol. The data that follow are typical of the results obtained.

Table 2 shows the flocculation values for different electrolytes with sol No. 1, dilutions being made with water. Table 3 shows the flocculation values for the same sol, dilutions being made with 95 per cent ethyl alcohol.

Table 4 and figure 1 show flocculation values for sol No. 2, dilutions being

TABLE 1

Data on preparation and properties of the two sols

SOL NO.	TIME OF DIALYSIS	TEMPERATURE OF DIALYSIS	CONCENTRATION OF CHROMIUM	RELATIVE VISCOSITY	pH	PURITY
	hours	*degrees C.*	*grams per liter*			
1	48 48	80 60	0.814	1.580	3.7	Slight precipitate with $AgNO_3$
2	96	85	0.769	Too viscous to measure	6.1	No precipitate with $AgNO_3$

TABLE 2

Flocculation values for different electrolytes with sol No. 1

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	1.4	1.8	2.2	2.7
KCl	1.5	1.7	2.3	2.7
$BaCl_2$	0.9	1.3	1.6	1.9
Na_2SO_4	0.05	0.06	0.05	0.06
Na_3PO_4	0.03	0.03	0.03	0.02

TABLE 3

Flocculation values for different electrolytes with sol No. 1

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	1.4	1.7	1.9	2.3
Na_2SO_4	0.05	0.05	0.05	0.04
Na_3PO_4	0.03	0.03	0.03	0.03

TABLE 4

Flocculation values for different electrolytes with sol No. 2

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	0.3	0.9	1.5	2.2
KCl	0.4	0.9	1.4	2.3
$BaCl_2$	0.3	0.8	1.0	1.2
Na_2SO_4	0.04	0.04	0.04	0.04
Na_3PO_4	0.032	0.03	0.024	0.02

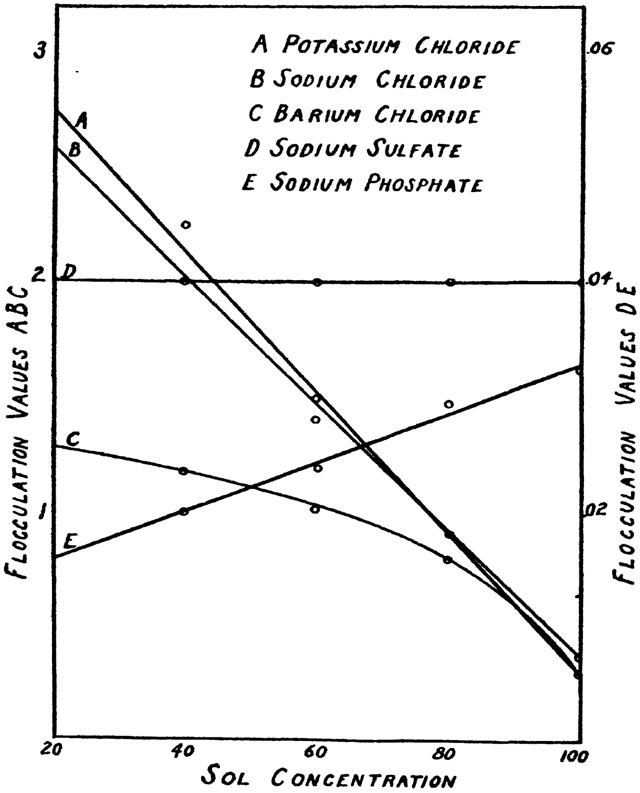

FIG. 1

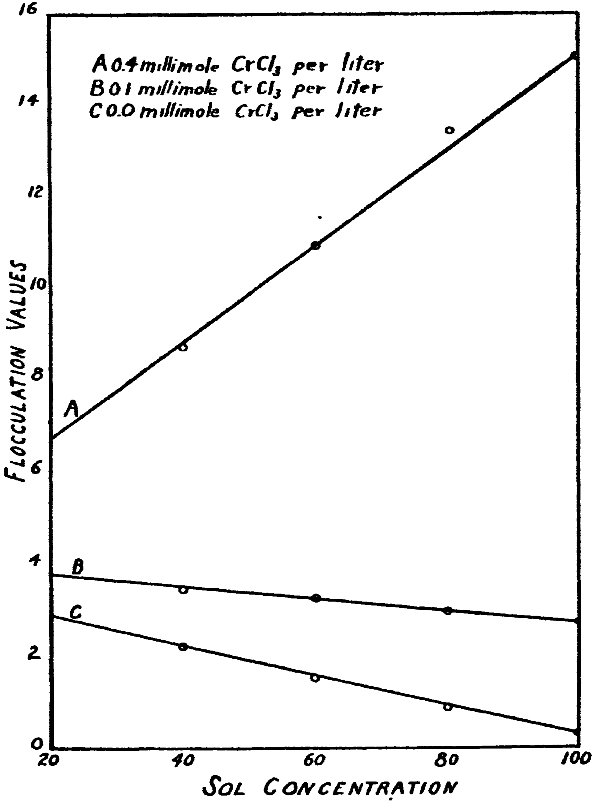

FIG. 2

FIG. 1. CHANGE OF FLOCCULATION VALUE WITH SOL CONCENTRATION
FIG. 2. SOL PURITY AND CHANGE OF FLOCCULATION VALUE

made with water. Table 5 shows flocculation values for the same sol, dilutions being made with 95 per cent ethyl alcohol.

Stock samples of sol No. 2 were made impure by adding respectively 0.1 and 0.4 millimoles of chromium chloride per liter. Dilutions were made with water and flocculation values for sodium chloride determined as above. The results are given in table 6 and figure 2.

TABLE 5

Flocculation values for different electrolytes with sol No. 2

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	0.3	0.7	0.5	0.04
Na_2SO_4	0.04	0.06	0.03	<0.001
Na_3PO_4	0.032	0.04	0.02	<0.001

TABLE 6

Flocculation values obtained with sol No. 2 and sodium chloride in the presence of chromium chloride

CHROMIUM CHLORIDE ADDED	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
millimoles				
0	0.3	0.9	1.5	2.2
0.1	2.7	3.0	3.2	3.4
0.4	15.0	13.4	10.5	8.8

DISCUSSION OF RESULTS

The purified sols follow the Burton-Bishop rule for all ions (tables 2 and 4, figure 1). When sufficient chromium chloride is added to the purified sols they fail to follow the rule for monovalent ions (table 6, figure 2). This fact, combined with the fact that the slope of the curve obtained when flocculation values are plotted against sol concentration (figure 2) varies with the purity of the sol, strengthens the conclusion (4) that the applicability of the Burton-Bishop rule is a function of sol purity.

When dilutions are made with alcohol the very highly purified sols (table 4) do not follow the Burton-Bishop rule for monovalent ions, but the less highly purified sols (table 2) do. The stability of chromic hydroxide hydrosols is due to hydration as well as ion adsorption. In the very highly purified sol the rôle of hydration is probably relatively great; in the less highly purified sol it is relatively small. Alcohol is a dehydrating agent; accordingly it will sensitize and even coagulate a hydrated sol (1). When a very highly purified sol is diluted with alcohol, the relative dehydrating effect may be so great and the sensitization so acute that the Burton-Bishop rule does not function. When a less highly purified sol which owes less of its stability to hydration is diluted with alcohol, the sensitization produced by dehydration is so slight compared to the initial stability due to ion adsorption that the dilution effect still follows the Burton-Bishop rule.

SUMMARY

The applicability of the Burton-Bishop rule to chromium hydroxide hydrosols is a function of the purity of the sol; highly purified sols follow the rule, impure sols do not.

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THE DIFFUSION COEFFICIENTS OF MOLECULES AND IONS FROM MEASUREMENTS OF UNDISTURBED DIFFUSION IN A STATIONARY MEDIUM

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Numerous measurements of the rate of penetration of dissolved substances into diffusion media have been made. The work of Stiles (2), who used an indicator for determining the rate of penetration of electrolytes into gels, illustrates a simple and direct type of experimental method for such measurements. However, the results of many such measurements have been expressed by means of empirical equations which do not permit the calculation of diffusion coefficients. The various equations which have been derived for the calculation of diffusion coefficients appear either to be inapplicable to this particular type of experimental method, or to involve a complicated and sometimes questionable method of calculation. This is particularly true of the calculation of the diffusion coefficient of an individual ion of an electrolyte in solution.

The purpose of the present paper is to present a simple mathematical basis for such methods, and to point out a relationship between the distance of penetration and the diffusion coefficient which should be useful for measurements with solutions.

DIFFUSION OF UNCHARGED PARTICLES

If a diffusing particle is placed in the center of a tube of motionless diffusion medium of indefinite length at zero time, then the probability curves for the position of the particle at later times are shown in figure 1a. These probability curves are expressed by the well-known Gaussian equation,

$$y = \frac{1}{q(2\pi)^{\frac{1}{2}}} e^{-\frac{X^2}{2q^2}} \tag{1}$$

where $y\mathrm{d}X$ is the probability of the particle being in any given section, $X - X + \mathrm{d}X$, in the diffusion medium and q is a function of the diffusion coefficient D and the time t.

This family of curves represents also a family of concentration curves if a large number of diffusing particles are placed in the central section at zero time. Under such conditions the number of particles in any given section, $X - X + \mathrm{d}X$, is given at any time by

$$ny\,\mathrm{d}X = \frac{n}{q(2\pi)^{\frac{1}{2}}}\,e^{-\frac{X^2}{2q^2}}\,\mathrm{d}X. \tag{2}$$

Thus the concentration in this section is $ny = m$, and

$$m = \frac{n}{q(2\pi)^{\frac{1}{2}}}\,e^{-\frac{X^2}{2q^2}} \tag{3}$$

But q^2, the mean square deviation from the mean, is given by

$$q^2 = \frac{1}{n}\sum_{i=1}^{i=n}(X_i - \bar{X})^2 \tag{4}$$

where $\bar{X}$ is the mean distance traveled by the particles in time t. For uniform diffusion in both directions

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{i=n} X_i = 0 \tag{5}$$

and therefore

$$q^2 = \frac{1}{n}\sum_{i=1}^{i=n} X_i^2 \tag{6}$$

But this is the value of $\overline{\Delta x^2}$ in the equation of Einstein (1)

$$\overline{\Delta x^2} = \frac{1}{n}\sum_{i=1}^{i=n} X_i^2 = 2Dt \tag{7}$$

Substituting $2Dt$ for q^2 in equation 3,

$$m = \frac{n}{(4\pi Dt)^{\frac{1}{2}}}\,e^{-\frac{X^2}{4Dt}} \tag{8}$$

In this equation, m is the concentration of diffusing particles at any distance X from the central section at any time t, $\frac{n}{(4\pi Dt)^{\frac{1}{2}}}$ representing the concentration in the central section at that time.

If the concentration in the central section is kept constant at m_0, each ordinate in figure 1a will in effect be multiplied by a constant times $(4\pi Dt)^{\frac{1}{2}}$ and as a result a family of concentration distance curves as in figure 1b and equation 9 will be obtained.

$$m = m_0 e^{-\frac{X^2}{4Dt}} \tag{9}$$

or

$$\frac{X^2}{4Dt} = \ln m_0 - \ln m \tag{10}$$

or for any given constant value of m $(= m')$

$$D = \frac{X^2}{4t}\,\frac{1}{\ln m_0 - \ln m'} \tag{11}$$

Thus the value of the diffusion coefficient may be determined, m_0 being the concentration in the central section and X being the distance from the central section at which the concentration is m' at time t.

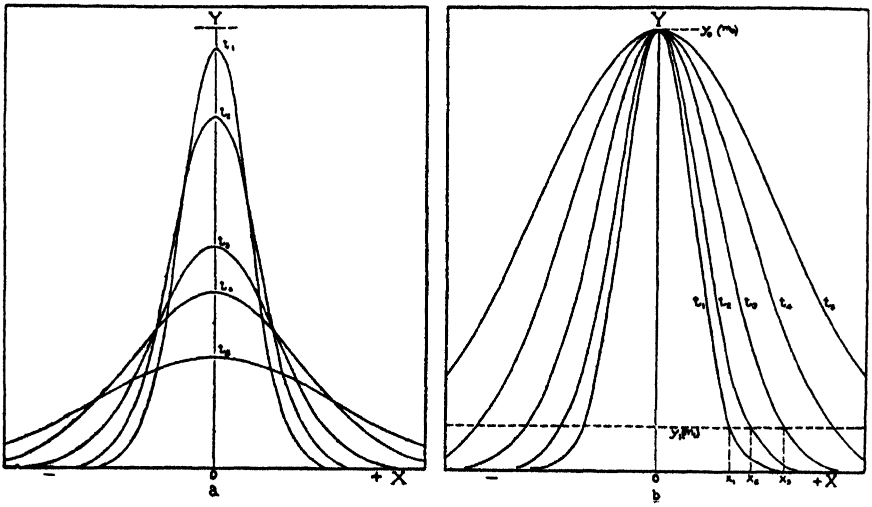

FIG. 1. CONCENTRATION-DISTANCE CURVES FOR UNDISTURBED DIFFUSION

DIFFUSION OF CHARGED PARTICLES

If the diffusing particles are ions, the distance of penetration due to normal diffusion X will differ from the experimentally determined distance X_a by the amount X_e, where X_e is the distance migrated by the ions due to the potential gradient resulting from the diffusion potential E. For very small values of m', we may assume that the diffusion potential in the system is distributed uniformly over the distance X_a, and the velocity of migration is therefore

$$\frac{dX_e}{dt} = U\frac{E}{X_a} \tag{12}$$

where U is the mobility of the diffusing ion. Since both this velocity and the velocity due to normal diffusion are inversely proportional to the distance of the concentration m' from the central section, the sum of the two velocities $\left(\frac{dX_a}{dt}\right)$ must also be inversely proportional to this distance and therefore

$$\frac{X_a^2}{t} = k \tag{13}$$

Thus X_a^2 is proportional to the time, as has been observed by many investigators (2, 3, 4).

The value of X_e is given by

$$X_e = \int_0^t U \frac{E}{X_a} dt = \frac{2UE}{k^{\frac{1}{2}}} t^{\frac{1}{2}} \tag{14}$$

Therefore

$$X = X_a - \frac{2UE}{k^{\frac{1}{2}}} t^{\frac{1}{2}} = \left(1 - \frac{2UE}{k}\right) X_a \tag{15}$$

Substituting the values of X and k into equation 11

$$D = \frac{X_a^2}{4t}\left(1 - \frac{2UE}{\frac{X_a^2}{t}}\right)^2 \frac{1}{\ln m_0 - \ln m'} \tag{16}$$

Equation 16 reduces to equation 11 if the diffusing particles are uncharged or if the diffusion potential is zero.

Preliminary results of colorimetric measurements of the penetration of cupric chloride into gels indicate that the equations suggested are useful and accurate.

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THE HEATS OF ADSORPTION OF CERTAIN ORGANIC VAPORS ON ACTIVATED CHARCOAL AT 25°C. AND 50°C.[1]

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The heat evolved on contact of a vapor with an adsorbent is one of the most important and characteristic quantities associated with the adsorption phenomenon. It has been calculated most generally from the slopes of the isosteres. McBain (12), however, claims that this method is physically impossible when the saturation values are different at different temperatures and an amount of sorption within the range of saturation values is under consideration. The basis of this claim is the fact that the equation involved,

$$\frac{d \ln p}{dT} = -\frac{q}{RT^2}, \quad \text{or} \quad \frac{d \ln p}{d(1/T)} = \frac{q}{R}$$

applies quite strictly also when the saturation pressure is just exceeded and liquid is being condensed. In general (6), it has been found that the heats of adsorption thus calculated are usually lower than those experimentally determined.

The refinements in the use of the ice calorimeter first made by Lamb and Coolidge (6), and later by Marshall and Bramston-Cook (11), have made this instrument a means of precise measurement of the heat of adsorption. Gregg (4) has employed both the ice calorimeter and the phenol calorimeter at 40.36°C. Employing a copper calorimeter similar to that used in measuring heat capacities at low temperatures, Magnus and his coworkers (9, 10) have measured the heat of adsorption of carbon dioxide on charcoal at 0°C. and 25°C.

In spite of the accuracy attainable, the use of the ice calorimeter involves one serious disadvantage in that most ordinary vapors may exist as liquids at 0°C., and hence the heat liberated may be in part a heat of condensation. These condensation effects may be entirely eliminated at high temperatures by the use of the apparatus designed by Pearce and McKinley (14) and later used by the present authors (15). Temperature changes are measured by a 24-junction thermoelement, and the apparatus is suitable for any temperature for which satisfactory calorimeter liquids are available.

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[1] This paper is a brief extract of a dissertation presented to the Graduate Faculty of the State University of Iowa by George H. Reed in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

TABLE 1

The heats of adsorption of methyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.433	11.17	4.95	4.95	0.423	0.322	9.24	4.08	4.08	0.442
1.021	21.01	3.95	8.91	0.401	0.932	18.58	4.04	8.12	0.433
1.748	29.11	3.10	12.01	0.383	1.695	25.39	2.59	10.71	0.380
3.202	41.34	4.69	16.70	0.384	2.612	32.88	3.16	13.87	0.422
1.120	8.57	3.94	3.94	0.460	3.781	39.95	3.12	16.99	0.441
2.475	15.79	2.86	6.80	0.396	0.401	10.60	4.80	4.80	0.453
3.864	21.79	2.57	9.37	0.428	1.254	20.40	3.96	8.76	0.404
5.955	29.66	3.32	12.69	0.422	2.111	27.86	3.21	11.79	0.430
9.312	39.08	3.65	16.34	0.388	3.102	34.35	2.46	14.43	0.379
					4.960	43.63	3.65	18.08	0.393
$h = 0.4887X^{0.9545}$; $\Delta = 0.15$					$h = 0.4820X^{0.9600}$; $\Delta = 0.13$				

TABLE 2

The heats of adsorption of ethyl and n-propyl chloride vapors at 50°C.

ETHYL CHLORIDE					*n*-PROPYL CHLORIDE				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.040	7.85	5.06	5.06	0.645	1.903	1.28	1.10	1.10	0.859
0.144	15.73	4.65	9.71	0.590	4.614	3.15	1.54	2.64	0.824
0.273	22.83	3.53	13.24	0.497	8.310	5.54	1.68	4.32	0.703
0.441	30.03	3.71	16.95	0.515	14.644	8.23	1.41	5.73	0.524
0.709	37.43	3.62	20.57	0.490	1.328	1.43	1.19	1.19	0.832
1.090	44.32	3.18	23.75	0.462	2.914	3.36	1.45	2.64	0.751
0.347	8.21	4.45	4.45	0.542	5.367	5.95	1.88	4.52	0.726
0.808	15.38	4.36	8.81	0.608	7.914	7.79	1.37	5.89	0.745
1.283	22.02	4.42	13.23	0.666	10.991	10.39	1.70	7.59	0.654
1.873	28.20	2.87	16.10	0.464	13.692	12.69	1.55	9.14	0.674
2.750	35.40	4.05	20.15	0.362					
$h = 0.7534X^{0.9150}$; $\Delta = 0.30$					$h = 0.8790X^{0.9220}$; $\Delta = 0.07$				

Garner and his coworkers (1, 3, 13) have devised an adiabatic calorimeter employing two thermoelements. With this they have measured the heat of adsorption of oxygen on coals and charcoals at temperatures between

TABLE 3

The heat of adsorption of isopropyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	9.02	4.80	4.80	0.532	0.000	7.74	4.58	4.58	0.592
0.040	17.07	4.93	9.73	0.612	0.079	16.98	5.74	10.32	0.621
0.055	24.85	4.80	14.53	0.617	0.233	25.22	4.82	15.14	0.585
0.070	31.96	3.95	18.48	0.556	0.317	32.14	4.34	19.48	0.627
0.075	40.25	4.90	23.38	0.591	0.491	39.99	4.65	24.13	0.592
0.100	48.14	4.57	27.95	0.579	0.045	5.44	3.35	3.35	0.616
0.000	7.09	3.91	3.91	0.552	0.050	12.56	3.89	7.24	0.546
0.060	15.76	5.61	9.52	0.647	0.055	19.48	4.44	11.68	0.642
0.065	22.20	3.75	13.27	0.582	0.094	27.24	4.81	16.49	0.621
0.075	30.60	4.63	17.90	0.551	0.159	34.28	4.10	20.59	0.582
0.095	39.08	4.53	22.43	0.534	0.248	43.05	4.95	25.54	0.564
0.124	46.96	4.01	26.44	0.509					
$h = 0.6412X^{0.9720}$; $\Delta = 0.26$					$h = 0.6398X^{0.9820}$; $\Delta = 0.14$				

TABLE 4

The heat of adsorption of n-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	6.98	5.03	5.03	0.721	0.000	4.27	3.49	3.49	0.817
0.000	12.06	3.61	8.64	0.711	0.000	10.02	3.56	7.05	0.619
0.000	21.38	6.52	15.16	0.700	0.025	15.42	4.14	11.19	0.767
0.000	26.56	3.58	18.74	0.691	0.030	22.87	5.22	16.41	0.701
0.000	31.72	3.58	22.32	0.694	0.069	30.17	4.79	21.20	0.656
0.000	40.63	6.05	28.37	0.679	0.114	37.71	5.26	26.46	0.698
0.000	5.13	3.59	3.59	0.700	0.203	45.09	5.07	31.53	0.687
0.000	10.52	3.86	7.45	0.716	0.773	62.10	12.06	43.59	0.709
0.000	15.80	3.74	11.19	0.708	0.000	5.95	4.55	4.55	0.765
0.000	29.07	9.34	20.53	0.704	0.000	13.49	5.26	9.81	0.698
0.000	34.32	4.06	24.59	0.773	0.000	23.77	7.36	17.17	0.716
0.000	39.16	2.62	27.21	0.541	0.070	29.12	3.18	20.35	0.594
0.025	50.70	7.66	34.87	0.664	0.075	35.38	4.39	24.74	0.701
					0.110	43.19	4.98	29.72	0.638
$h = 0.7925X^{0.9640}$; $\Delta = 0.15$					$h = 0.7905X^{0.9690}$; $\Delta = 0.23$				

18°C. and 450°C. Observations made in their experiments have shown that on admission the oxygen is first adsorbed on the outside layers of the charcoal. The rate of adsorption is so rapid that with small volumes of gas no oxygen penetrates the interstices between the grains to the charcoal around the thermoelement. For this reason the surfaces of capillaries

TABLE 5

The heats of adsorption of secondary-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.635	2.04	1.35	1.35	0.662	0.728	2.84	1.89	1.89	0.666
1.758	4.88	1.91	3.26	0.673	1.378	5.11	1.10	2.99	0.485
2.719	6.93	1.35	4.61	0.659	1.977	6.73	1.13	4.12	0.698
3.745	9.03	1.35	5.96	0.643	3.147	9.96	2.23	6.35	0.690
4.875	11.20	1.41	7.37	0.650	4.772	13.26	2.41	8.76	0.730
1.265	1.71	1.16	1.16	0.678	6.388	16.26	1.86	10.62	0.620
2.211	2.86	0.74	1.90	0.644	0.803	2.68	1.88	1.88	0.702
3.610	4.10	0.86	2.76	0.694	1.467	4.44	1.14	3.02	0.648
5.174	5.41	0.83	3.59	0.634	2.250	6.38	1.02	4.04	0.526
8.176	7.78	1.42	5.01	0.599	3.097	8 42	1.36	5.40	0.667
$h = 0.6775X^{0.9890}$; $\Delta = 0.03$					$h = 0.6699X^{0.9890}$; $\Delta = 0.14$				

TABLE 6

The heats of adsorption of tertiary-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	5.20	3.50	3.50	0.673	1.715	1.83	1.23	1.23	0.671
0.000	11.56	4.01	7.51	0.631	3.105	3.11	0.77	2.00	0.602
0.070	17.87	3.80	11.31	0.602	5.129	5.01	1.29	3.29	0.679
0.110	24.30	4.01	15.32	0.624	9.515	7.21	1.51	4.80	0.686
0.179	29.37	3.03	18.35	0.598	12.944	10.10	1.72	6.52	0.595
0.000	5.68	3.80	3.80	0.669	17.731	13.32	2.21	8.73	0.686
0.065	11.51	3.44	7.24	0.590	1.219	1.65	1.14	1.14	0.691
0.139	17.11	3.47	10.71	0.620	1.977	2.77	0.74	1.88	0.661
0.214	22.10	2.83	13.54	0.567	2.701	3.53	0.55	2.43	0.724
0.433	29.46	4.33	17.87	0.588	4.034	5.18	1.05	3.48	0.636
0.483	35.24	3.92	21.79	0.678	5.629	6.73	1.08	4.56	0.697
$h = 0.7096X^{0.9610}$; $\Delta = 0.13$					$h = 0.7064X^{0.9650}$; $\Delta = 0.06$				

lying nearest to the surface are the first to be saturated with oxygen. The very small, not easily accessible capillaries are not reached by the first admissions of gas. To meet these difficulties the original apparatus has since been modified (2) in such a way that the gas must first pass directly to the center of the charcoal and then diffuse through it to the outer wall of the gauze cylinder. The intimate contact between the fine grains of charcoal and the wire spirals of our adsorption bulbs justifies us in believing that the same conditions are equally met in the method that we have used.

We now present a brief report of the results obtained in a study of the heats of adsorption of a number of alkyl chloride vapors on activated charcoal at 25°C. and 50°C. The complete apparatus, its capabilities and technique, as well as the charcoal used are described in the previous paper (15).

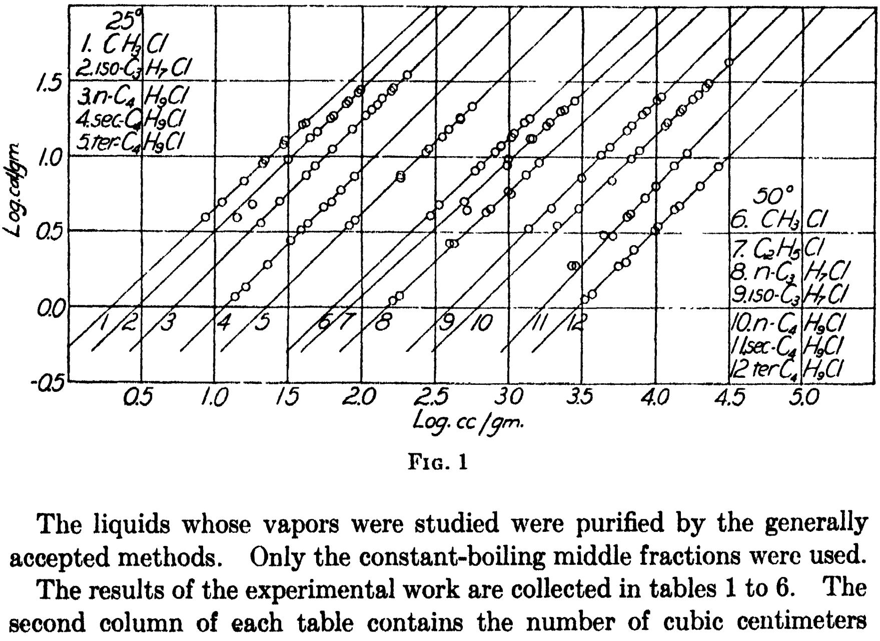

FIG. 1

The liquids whose vapors were studied were purified by the generally accepted methods. Only the constant-boiling middle fractions were used.

The results of the experimental work are collected in tables 1 to 6. The second column of each table contains the number of cubic centimeters (N. T. P.) of vapor adsorbed by 1 g. of charcoal under the equilibrium pressure given in column one. The third column contains the observed heat effects, d*h*; the total heats of adsorption, *h*, are given in column four. In the last column are the differential heats of adsorption in calories per cubic centimeter of gas per 1 g. of charcoal. The data given in these tables represent two or more series; they have been obtained with various weights of charcoal, some fresh and others previously used, and with variation in the rate of admission to the charcoal.

Lamb and Coolidge (6) have found that chlorine-containing vapors poison charcoal in such a way that the heat of adsorption decreases in successive runs on the same sample of charcoal. This poisoning effect did not appear in our work. The heat of adsorption has been found to be independent of previous use, if the used sample is outgassed at 550°C. to a pressure of 0.0001 mm.

The data are represented in the curves of figure 1. These have been successively displaced to the right by definite intervals to avoid superposition. The curves are rectilinear and are represented by the relation

$$\log h = \log m + n \log X$$

where h is the number of calories liberated when X cc. of vapor are adsorbed by 1 g. of charcoal, n is the slope, and log m is the value of the intercept at unit concentration. The constants are indicated in the empirical equations to be found at the bottom of the different tables. It is interesting to note that the values of m and n for any one vapor are very nearly identical at the two temperatures. The values for the total heats of adsorption calculated with the aid of these equations are in good agreement with the values found experimentally. The average deviation, Δ, between the observed and calculated values, is for the most part within the limits of accuracy of the experiment.

It appears to have been definitely proved to many interested in adsorption that the heat of adsorption of a gas or vapor by charcoal does vary considerably with the temperature. This view is fully supported by researches upon the heat of adsorption of oxygen and carbon dioxide by charcoal at different temperatures.

Garner and his coworkers (1, 3, 13) have found that for an oxygen concentration of 1.5×10^{-4} moles per gram of charcoal the heat of adsorption increases from 70,000 cals. at 18°C. to somewhat more than 115,000 cals. at 200°C., and it finally attains a value of 224,000 cals. at 450°C. Thus, we find the heat of adsorption of oxygen on charcoal to be approximately equal to the heat of formation of carbon dioxide at a temperature not far above 100°C. That they are not dealing with a case of simple reversible adsorption, but rather, possibly, with an activated adsorption or with a chemical surface reaction, is shown in part by their observation that when oxygen is heated in contact with charcoal to 100°C. only traces of carbon dioxide are evolved. With further increase in temperature carbon dioxide is formed in increasing quantity.

Long ago, Rhead and Wheeler (16) came to the conclusion that oxygen combines directly with charcoal to form a physicochemical complex, C_xO_y, which decomposes on heating to carbon dioxide and carbon monoxide. Their conclusion is completely confirmed by the work of Hulett and Lowry (7). The latter thoroughly outgassed their charcoal at 900°C. to 1000°C., allowed it to cool to room temperature in a vacuum, and then admitted various gases. They found it possible to recover 90 per cent of the carbon dioxide and a smaller percentage of water at room temperature, but both were completely recovered at 184°C. Gases like hydrogen, nitrogen, and carbon monoxide were completely recovered at room temperature. Oxygen, however, behaved very differently. After being admitted to the charcoal and allowed to come to equilibrium, only about one-half of the oxygen was recovered by evacuating at room temperature, and only traces of oxygen were obtained by heating the charcoal to 184°C. Upon increasing the temperature still further the oxides of carbon began to appear, but not until a temperature of 900°C. to 1000°C. was reached did they recover all of the oxygen admitted. And then it was not oxygen, but a mixture of the oxides of carbon.

Magnus and Braner (8) have studied the heat of adsorption of carbon dioxide on charcoal at 17°, 27°, and 37°C. They have found that at constant temperature the heat of adsorption decreases with increase in pressure; furthermore, it decreases with rise in temperature at constant pressure.

In spite of the fact that Lowry and Hulett found it possible to remove only 90 per cent of their carbon dioxide, Shah (17) states that there is no indication of a chemical interaction between charcoal and oxygen at ordinary temperatures. He did find, however, that not until the temperature is raised to 200°C. does carbon dioxide begin to be slowly reduced.

Keyes and Marshall (5) have studied the adsorption of oxygen, chlorine, carbon dioxide, ammonia, and ether by charcoal at 0°C. Of these the behavior of oxygen was peculiarly striking. The log q–log c curve is not only not rectilinear, but it actually shows an inflexion. Only for the very low, and possibly for high oxygen concentrations, is there any direct proportionality between log q and log c. Although linear equations of these two variables represent the data of carbon dioxide fairly well, the curve shows a trend which is slightly convex to the log c axis. Chlorine and ammonia show a similar behavior. The curves for oxygen and ether, on the other hand, are concave to the log c axis. The log h–log c curves for the vapors studied in this work are rectilinear throughout.

It is evident from the work cited that oxygen and carbon dioxide do show very pronounced heats of adsorption on charcoal, and these vary markedly with increase in temperature. That these heat effects are modified in no uncertain degree by heat effects due to some kind of chemical interaction between the gas and the charcoal at the gas–solid interface appears most probable. The heats of adsorption should be expected, therefore, to be considerably different from those which would be obtained if the adsorption forces were of the van der Waals type only. It is the latter forces which appear to be involved in the adsorption of the vapors employed in this work.

The molecular heats of adsorption, h_m, calculated by the method employed in the previous paper (14), are collected in table 7. It will be observed that the heats of adsorption increase with increase in the length of the hydrocarbon chain. Also, that these heats are greater than those obtained for the branched chain compounds. Further, the difference between the molecular heats of adsorption for each vapor at the two temperatures is very small. This would indicate that the forces involved are those of van der Waals. The number of vapors studied is too small to make any general deductions regarding the effect of molecular complexity upon the heat of adsorption.

TABLE 7

The molecular heats of adsorption of alkyl chlorides at 25°C. and 50°C.

ALKYL CHLORIDE	MOLECULAR HEATS OF ADSORPTION		ISOSTERES
	At 25°C.	At 50°C.	
	kg-cals.	*kg-cals.*	*kg-cals.*
CH_3Cl	9.2	9.2	8.3
C_2H_5Cl	11.6*	12.2	10.6
n-C_3H_7Cl	15.0*	14.6	12.3
iso C_3H_7Cl	12.9	13.3	12.3
n-C_4H_9Cl	15.4	15.7	13.4
secondary C_4H_9Cl	14.5	14.4	
tertiary C_4H_9Cl	13.7	13.6	11.6

* From Pearce and McKinley (14).

SUMMARY

1. The heats of adsorption of certain alkyl chloride vapors on charcoal have been measured at 25°C. and 50°C. The heats of adsorption of ethyl chloride and *n*-propyl chloride have been determined at 50°C.

2. The molecular heats of adsorption at the two temperatures are of approximately the same magnitude. The temperature coefficient of adsorption between these temperatures is very small, if there is one at all.

3. The total heat of adsorption of any vapor increases apparently rectilinearly with the total amount adsorbed.

4. The molecular heat of adsorption of vapors with branched chains is always less than that of the vapors of the normal compounds at the same temperature. That of the normal compounds increases with increase in the length of the hydrocarbon chain.

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COMMUNICATION TO THE EDITOR

DENSITY OF WATER FROM VARIOUS SOURCES AND ISOTOPIC RATIO IN HYDROGEN

H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell, and H. V. A. Briscoe (J. Chem. Soc. **1934,** 1207) have determined the density of water with unquestionable accuracy. They have ascribed microchemical variation in the density of water from animal, vegetable, and mineral sources to the isotopic ratio in hydrogen in water.

W. D. Bancroft and L. P. Gould (J. Phys. Chem. **38,** 209 (1934)), as well as many others, have concluded that liquid water is a mixture of polymerized molecules coëxisting in reversible equilibrium. Emeléus and his coworkers made no mention of such a phenomenon. It seems worth while paying attention to the variation in polymerization of water molecules with rise of temperature in connection with so delicate a study of the isotopic ratio in hydrogen by means of the determination of the density of water. The question is to what extent the observed variation in density is influenced by polymerization and depolymerization with fall and rise in the temperature of water samples under the conditions of the experiment.

JITENDRA NATH RAKSHIT.

Ghazipur, U. P.,
India.

NEW BOOKS

Electrolytes. By HANS FALKENHAGEN. Translated by R. P. Bell. xvi + 348 pp. Oxford: Clarendon Press, 1934. Price: $9.50.

This book can be cordially recommended to the attention of physical chemists.

After a short discussion of ideal dilute solutions, the author gives a sketch of the "classical" theory of electrolytes as developed by Arrhenius. The anomalies in the thermodynamic properties and in the electrical conductance of strong electrolytes are pointed out. This is followed by a section devoted to the early theories proposed to account for the observed anomalies. The theory of Debye is then given in considerable detail in its application both to the thermodynamic properties of solutions and to their electrical conductance. The last three chapters are devoted to the modern theory of the viscosity of strong electrolytes, more concentrated solutions, and the statistical foundations of Debye's theory. The appendix contains a short paper, by R. H. Fowler, on recent applications of quantum mechanics to the theory of electrolytes.

The book contains numerous references to original sources. The index is entirely inadequate, but this defect is partly counterbalanced by an unusually detailed table of contents.

Students who desire to become acquainted with recent developments in the theory of electrolytes will find this book of great value.

F. H. MACDOUGALL.

Inorganic Colloïd Chemistry. By H. B. WEISER. 15.5 x 23.5 cm.; xi + 389 pp. New York: John Wiley and Sons, Inc., 1933. Price: $4.50.

Professor Weiser has done chemistry a great service by bringing together, for the first time in a critical survey, the colloidal behavior of the elements. Up to the present time many sources had to be consulted in order to assemble the material presented in this single volume. Not only does the author give the latest accepted methods for preparing the elements in the colloidal form, but he thoroughly discusses their properties as well as theories concerning their behavior in this state. General principles of colloid theory are sufficiently treated, together with biological and industrial applications, so that the book is useful both as a text and as a source book of information.

Following a chapter on the formation of the colloidal elements, the book is naturally divided into a section on the metallic elements and one on the non-metallic elements. As far as possible the elements are taken up in the order in which they appear in the periodic table. The section devoted to the metallic elements is completed by chapters on the adsorption of gases by metals and colloidal metals as contact catalysts. Covering about sixty pages these two chapters give the reader a remarkably complete picture of the present status of these important and expanding fields of investigation. In the section devoted to the non-metals the chapter on colloidal carbon appeared to the reviewer to be especially complete and well written.

The book is well illustrated and a very complete list of references to original work is given. An author as well as a subject index appears at the end of the book. Workers in the field will welcome this important addition to the growing list of publications, while graduate students will find that the book is very useful in giving them a reasonably complete survey of the subject.

L. H. Reyerson.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem. Edited by Wilhelm Eitel. Vol. VI. 21 x 29 cm.; 234 pp. Brunswick: Fried. Vieweg und Sohn, 1934. Price: 28 RM.

The Institute, under the direction of Dr. Wilhelm Eitel, continues to be very active in research, and the sixth volume of its collected papers contains much that is of scientific interest. Several investigations by H. E. Schwiete and H. Elsner von Gronow and colleagues deal with calcareous cements. Crystals from a Portland cement kiln in which small additions of fluorspar were made to the charge, and identified as alite, proved on analysis to consist of tricalcium silicate holding 4.5 per cent of tricalcium aluminate in solid solution; the fact that such solubility occurs was confirmed by x-ray examination, the lines of the compound being clearly discernible, but disappearing on heating the clinker. The specific heats of the principal compounds present in Portland cement have been determined from 20°C. to 1500°C., these data being required for the calculation of the heats of reaction in the kiln. Several other thermochemical investigations in this field have been completed, covering both the compounds present in clinker and those formed by hydration. A study of the development of heat during the setting of aluminous cement leads to the conclusion that the process is purely colloidal and is governed by the pH value, an increase in this value accelerating setting, whilst a diminution retards it. This conclusion requires to be controlled by other methods, such as microscopical and x-ray examination. A similar study of the setting of Portland cement also lays stress on gel formation as an essential part of the process.

The papers on glass include a long review of the constitution of glass by W. Weyl, in which the subject is reviewed as a whole, as well as an experimental investigation in which glasses were prepared under high oxygen pressure, with the object of retaining in solution the higher oxides which ordinarily dissociate. Alkali lead glass in this way forms plumbates, which evolve oxygen when the glass is fused under reduced pressure. Manganese may also be retained as the higher oxide, so that under pressure a deep violet glass has been prepared, containing only 0.1 per cent MnO. A series of studies of the flow of glass in various machine processes for the production of bottles and other objects is remarkable for the very beautiful series of photographs taken by the Schlieren method.

As usual, the volume contains accounts of several improvements in technique, which may be of interest to workers in other fields than that of the silicates.

C. H. Desch.

The Design and Use of Instruments and Accurate Mechanism (Underlying Principles). By T. N. Whitehead. 279 pp.; 85 figs. New York: The Macmillan Co., 1934.

The book is written for the designers of accurate scientific instruments such as, for example, comparators. But the discussion covers much more than this field. The author deals with the fundamental principles covering design and the use of the resulting devices. He therefore deals with the theory of errors of observation from the standpoint of the instrument and from the standpoint of the human nature of the observer. He admits the utility of mathematics in the expression of physical phenomena, but warns that the use of mathematics must be tempered by independent check of the physical facts. The aim in writing the book has been "to concentrate on those parts of the subject which seem to call for revision and with which mechanical designers are less likely to be acquainted." Anyone interested in the building of scientific instruments and of precision machines should read this volume.

GEORGE GLOCKLER.

The Kinetic Theory of Gases. Some Modern Aspects. By MARTIN KNUDSEN. Methuen's Monographs on Physical Subjects. 17 x 11 cm.; 64 pp. London: Methuen and Co., Ltd., 1934. Price: 2s. 6d.

This book embodies the material of three lectures given in 1933 in the University of London by its distinguished author. It is less a treatise on the kinetic theory than a summary of Professor Knudsen's own researches, but since these are concerned with several fundamental parts of the kinetic theory, the author has been able to make a connected story of the material. The simpler formulas are deduced, whilst the complicated are merely quoted. The apparatus is described and illustrated. The sections deal with the vapor pressure of mercury, evaporation and condensation, molecular flow through tubes, the cosine law, resistance to motion in gases, thermal molecular pressure, molecular heat conduction and coefficient of accommodation, and the absolute manometer. The treatment is clear and attractive, and the book is one which will be read with interest and profit by many kinds of readers.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59: Eisen, Teil A, Lieferung 6. 26 x 18 cm.; xxi + 1167–1420 pp. Berlin: Verlag Chemie, 1934. Price: 41.50 Marks. Subscription price: 36 Marks.

This volume contains a description of the systems composed of iron and the nonmetallic elements sulfur, selenium, tellurium, boron, and carbon. The treatment is on the lines of the phase rule, although in many cases the chemical properties of the compounds are dealt with in full. The section on the iron–carbon system, in view of its great technical importance, is very detailed, and the volume is essentially a monograph on carbon steels. Nitriding of iron is included. The technical and patent literature is exhaustively covered. The volume is one of exceptional interest and is a valuable summary of a very extensive literature.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59: Eisen, Teil A, Lieferung 7. 26 x 18 cm.; xxvi + 1421–1634 pp. Berlin: Verlag Chemie, 1934. Price: 36 Marks. Subscription price: 31.5 Marks.

This volume is concerned solely with the magnetic and electrical properties of iron and steel. The magnetic properties, which are of great technical importance, are very fully described, the section being introduced by a clear account of the general theory of ferromagnetism, including a discussion of the units, the names of which have recently been altered. The text is illustrated by a large number of diagrams and contains much numerical data. The electrical properties include conductivity, thermoelectric properties, contact potentials, discharges between electrodes, and electron emission. The volume is essentially of physical interest and constitutes a valuable monograph on the subjects with which it deals. The brief accounts of the various phenomena dealt with from the general point of view, and the definitions of the various magnitudes concerned in the effects, will be found very useful for reference by chemists, and the inclusion of x-ray data and lattice constants is a valuable feature.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 1. 26 x 18 cm.; iv + 284 pp. Berlin: Verlag Chemie, 1934. Price: 42 Marks. Subscription price: 38 Marks.

This volume deals with the occurrence, production, and physical properties of metallic aluminum. The section on its occurrence includes an account of the aluminum minerals, including silicates, and contains a long section on bauxite and laterite, which are used in the technical production of the metal. The section on the production of the metal deals briefly with the older chemical methods and in detail with the electrolytic processes now in use, and with refining processes. The forms of commercial aluminum are described. The physical properties are classified under the headings atomic, crystallographic, mechanical, thermal, optical, magnetic and electrical, and in the descriptions a large amount of numerical data is collected. The volume provides a very exhaustive and authoritative account of aluminum metal both from the physical and chemical aspects, although the description of the purely chemical properties belongs to a later issue. The references are very complete and the literature, which is brought well up to date, is international.

J. R. PARTINGTON.

The Adsorption of Gases by Solids. By S. J. GREGG. 17 x 11 cm.; viii + 120 pp. London: Methuen and Co., Ltd., 1934. Price: 2s. 6d.

The subject of adsorption of gases by solids is one of great complexity and interest, and some reasoned survey of the present state of affairs was much in need. A recent volume published by the Faraday Society indicated that the interest was there, and Mr. Gregg has in small compass given us a detached survey of the subject, admirable in its grasp of essentials and breadth of scope. It is a pity therefore that the series of monographs to which the book belongs has made it necessary to deal with many aspects in only a very brief way. Perhaps when agreement has been reached on some of the more controversial items, Mr. Gregg will undertake a larger survey. In the meantime he has managed to pack into one hundred and twenty small pages nine chapters on general characteristics, experimental methods, heats of adsorption, theories, adsorption forces, adsorption layers, surface structure, activated adsorption and, finally, chemisorption. In addition each chapter has its own bibliography, guiding readers to the original papers of importance. The author's interest has perhaps centred on the explanations of the many results obtained rather than on experimental method, to which only a little over two pages have been devoted. In common with other writers on adsorption, Mr. Gregg has failed to make reference to the practically important process of clean-up, whereby gases are retained at the gettered glass surfaces of vacuum lamps and wireless valves. In spite of this blemish Mr. Gregg's book is a well thought out little volume and is worth a good deal more than the very reasonable price the publishers ask for it.

J. T. RANDALL.

Oberflächenspannung in der Biologie und Medizin. By FERDINAND HERCIK. 15 x 22 cm.; xii + 220 pp. Dresden and Berlin: Steinkopff, 1934. Price: unbound, 14 M; bound, 15 M.

This small volume deals essentially with the changes in surface tension caused by the solution of materials mainly of biological processes. Great emphasis is laid upon the utility of the ring method for determining these changes, a view with which many investigators would in all probability not agree. The data of Du Noüy are cited in extenso. These data on the surface tensions of dilute solutions present the interesting feature of exhibiting a series of minima at what are believed to be critical concentrations. From these minima Du Noüy and his coworkers have computed molecular dimensions which in some cases are in fair agreement with those obtained by other methods. It is somewhat remarkable that no such peculiarities are observed in the Langmuir trough, and it would seem eminently desirable for a series of parallel experiments to be carried out under identical conditions. A brief account is given of the relationships suggested between capillary activity and various other properties, such as enhancement of membrane permeability, increased sensitivity in the precipitin reaction, and the rates of sedimentation of red blood cells and erythrocytes. It is clear both from the divergencies in views expressed by various workers in these fields, as well as the lack of uniformity in the experimental results, that this is a fertile field ready to be cultivated by those who possess both the requisite physicochemical and biological experience.

ERIC K. RIDEAL.

German-English Chemical Terminology. An Introduction to Chemistry in English and German. By A. KING and H. FROMBERG 21 x 13 cm.; xvii + 324 pp. London: Thomas Murby and Co., 1934. Leipzig: Max Weg, 1934. Price: 12s. 6d.

The method of this book is the use of English on each left-hand page with German on the right. The subject matter has been selected, from well-known textbooks of both languages, so as to be representative of chemistry as a whole. Original and translation can be compared paragraph by paragraph, and the general accuracy can be relied on, since the book is the joint work of an English and a German chemist. The other feature of this book is the printing in italics of corresponding terms of both languages on their first appearance in the text, with also an index of these at the end.

The series has been started with geology; under the general editorship of Dr. W. R. Jones, other sciences are to follow.

The claim made that such books may be equally useful to both English and German students and that the use of dictionaries is avoided is probably true, provided that each knows something of the other language. It must be remembered that exact translation is not always possible, and that it is often an equivalent which is rendered in the other language. With this in mind such books should prove very useful.

W. H. PATTERSON.

Bilder zur qualitativen Mikroanalyse anorganischer Stoffe. By W. GEILMANN. 23 x 16 cm.; xii + 80 pp. Leipzig: Leopold Voss, 1934. Price: 8 RM.

In view of the increasing employment of microchemical tests in qualitative analysis, the present small atlas of photomicrographs comes as a useful addition to the analyst's library. The work contains close on two hundred and fifty illustrations, reproduced from actual photomicrographs obtained by the author, showing the characteristic forms of the crystals and crystalline precipitates resulting from the various microchemical tests, details of which are briefly given.

The difficulty that in the case of many reactions the appearance of the precipitate formed is liable to vary considerably with the concentration of the interacting solutions, etc., has been met by including in such cases two or more separate illustrations of the precipitates in question, showing their appearance when formed under differing conditions, and thus facilitating their identification.

A number of illustrations are also given of certain precipitates, such as zinc ammonium phosphate, which although not in themselves of value as a means of identification, are liable to be formed during the testing of mixtures, and may easily be misinterpreted.

A full index is provided, and the book is well printed, with clear and good illustrations.

H. F. HARWOOD.

Ergebnisse der exakten Naturwissenschaften. Sonderabdruck aus Bd XIII. Über den ausseren Photoeffekt an adsorbierten Schichten. By R. Suhrmann. 23 x 16 cm.; 74 pp. Berlin: J. Springer, 1934. Obtainable only in complete issue. Price: unbound, 28 RM; bound, 29.40 RM.

In this section of the *Ergebnisse* Dr. Suhrmann has given a survey of work on measurements of the external photoeffect for adsorbed layers. The outlook of the survey is for the most part experimental, and apparatus and results are illustrated in sixty-four diagrams. Until very recently the necessity for a really first class vacuum technique in work of this kind was not universally appreciated. As a result much of the older work is of little value. Dr. Suhrmann, however, steers a careful course through the maze of results available. After a preliminary historical survey he deals very briefly with the fundamental photoelectric laws. Many aspects of adsorbed layer problems are dealt with in the main section of the report, and of these we may mention the influence of gases and of outgassing technique on the photoelectric properties of the layers, the properties of adsorbed metal films, such as cesium on tungsten, the effects of temperature and of the electric field. Over two hundred references to original papers are appended.

J. T. Randall.

Ergebnisse der exakten Naturwissenschaften. Sonderabdruck aus Bd XIII. Elektrische Leitfähigkeit elektronischer Halbleiter. By B. Gudden. 23 x 16 cm.; 33 pp. Berlin: J. Springer, 1934. Obtainable only in complete issue. Price: unbound, 28 RM; bound, 29.40 RM.

Semiconductors have long been one of the mysteries of physics, but during the last year or two the general advances of quantum mechanics have gone far towards sketching in the main outlines of the fundamental conducting mechanism in these bodies. These theoretical advances are for the most part due to A. H. Wilson and R. H. Fowler, but a great deal of fundamental experimental work has been done by Gudden and Pohl from 1920 onwards. The work of greatest importance has been done on single crystals, such as zinc blende, while much of practical import has been carried out on copper oxide, selenium, and the associated rectifying contacts. The general division of work falls naturally into two classes. On the one hand there are single crystals, on the other powdered crystals, and both these types have been investigated with and without the stimulation of incident light. In the present reprint Professor Gudden has not attempted an exhaustive survey of the subject, but all who wish to obtain a good idea of the experimental results and their interpretation will do well to consult it, for it is written in a clear and simple way and is confined to main issues. The main items dealt with in the survey are: the existence of ionic or electronic conduction in semiconductors; the validity of Ohm's Law and the question of specific conductivity; the effect of temperature on the conductivity; photoelectric effects; and an outline of modern theory. A point of interest to chemists is the fact that the physical properties of semiconductors are largely dependent on impurities which may frequently be difficult or impossible to detect by ordinary chemical means.

J. T. Randall.

CONTRIBUTION TO THE THEORY OF SURFACE CONDUCTIVITY AT SOLID-LIQUID INTERFACES[1, 2]

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The double layer theory of Otto Stern may be briefly summarized as follows (7, 12, 14). The theory of Helmholtz gives values for the capacity of the double layer which agree approximately with those obtained from electrocapillary experiments. However, owing to kinetic heat motion, the double layer ions facing the liquid cannot have the distribution postulated by Helmholtz. On the other hand, Gouy's (6) theory, which is based on the existence of a diffuse double layer, gives values for the capacity which are far too great. Stern develops his concept of the double layer in this manner: under the influence of the electrostatic forces of the wall, one type of ion forms a sheet of charges of constant density ($-\sigma_0$) directly on the surface of the solid phase (inner Helmholtz layer). A sheet of positive charges ($+\sigma_0$) (outer Helmholtz layer) would be located at a distance δ from the negative layer providing the kinetic heat motion did not exist, say at a temperature of zero degrees absolute. At room temperature this charge will acquire a certain depth. A fraction, $+\sigma_1$, of the positive charges will face the sheet of negative ions, the rest ($+\rho$, in a column of liquid of 1 cm.^{2} cross section) extends into the interior of the solution with an asymptotically decreasing charge density (diffuse layer).

$$\sigma_0 = \sigma_1 + \rho$$

The electrokinetic potential, ζ, is the potential drop across the mobile component of the positive layer. According to Gouy all of the double layer ions, except those on the wall, are mobile with respect to hydrostatic forces, while according to Stern both sheets of ions comprising the Helmholtz layer are immobile with respect to hydrostatic forces.

In the present communication the equation for surface conductivity is developed, based on the layer of Stern, so as to include not only the diffuse

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[1] Presented before the Eleventh Colloid Symposium held at Madison, Wisconsin, June 14–16, 1934.

[2] The work reported in this paper has been aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

layer ions, but also those of the outer Helmholtz layer.[3] The equation thus becomes applicable to concentrated solutions, in which the surface conductivities predicted by the double layer theories of Stern, on the one hand, and of Gouy, on the other, would be expected to show a more marked disagreement. By comparison with experimental surface conductivity values, it should then be possible to choose between the theories.

The following cases are theoretically possible: (A) The ions attached to the wall possess no electrical mobility. The surface conductivity is due to those components of the double layer which lie in the liquid phase. Electrosmose, by increasing the velocity of double layer ions, these being carried along by the moving column of liquid, will increase surface conductivity. Case A would be expected to occur when the conductivity is determined with D. C. (B) The same as case A, except that no electrosmose occurs.[4] (C) All double layer ions, including those on the wall, conduct;

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[3] The simplified equation proposed last year (J. Phys. Chem. **36**, 3157 (1932)) did not include the Helmholtz layer ions, nor an electrosmotic correction. It agrees with equation 20, independently derived by Bikerman (Z. physik. Chem. **163A**, 378 (1933)), except for the mobility factor. Bikerman's equation 20 is as follows:

$$\text{(a) Surface conductivity per 2 cm}^2\text{.} = \Delta_c\, l_c + \Delta_a l_a$$

l_a and l_c are the ionic mobilities of cation and anion, while

$$\text{(b) } \Delta_c = \sqrt{\frac{2DRTc}{\pi F^2}}\left\{e^{\frac{F\zeta}{2RT}} - 1\right\}$$

$$\text{(c) } \Delta_a = \sqrt{\frac{2DRTc}{\pi F^2}}\left\{e^{\frac{-F\zeta}{2RT}} - 1\right\}$$

For potassium chloride, since $l_a = l_c$

$$\text{(d) Surface conductivity per 1 cm}^2\text{.} = \sqrt{\frac{DRT}{2\pi F^2}}\, c\left\{e^{\frac{F\zeta}{2RT}} + e^{\frac{-F\zeta}{2RT}} - 2\right\} l_c$$

$$\text{(e) Surface conductivity per 1 cm}^2\text{.} = \sqrt{\frac{DRT}{2\pi F^2}}\, c\left\{e^{\frac{F\zeta}{4RT}} - e^{\frac{-F\zeta}{4RT}}\right\}^2 l_c$$

If $e^{\frac{-F\zeta}{4RT}}$ can be neglected—large ζ —

$$\text{(f) Surface conductivity per 1 cm}^2\text{.} = \sqrt{\frac{DRT}{2\pi F^2}}\, c\, e^{\frac{F\zeta}{2RT}} \cdot l_c$$

[4] The surface conductivity measurements reported below were carried out with 1000-cycle A.C. From The Svedberg and Hugo Anderson's paper on electrophoresis (Kolloid-Z. **24**, 156 (1919)), we have drawn the conclusion that no significant electrosmose is likely to occur at this frequency. If this conclusion is correct the attempt made by some authors to explain A.C. surface conductivity data by the von Smoluchowski equation—which is equivalent to the electrosmotic component of surface conductivity—is meaningless.

there is electrosmose. (D) All double layer ions conduct; there is no electrosmose.

The experimental data do not permit a clean-cut choice between A–C, B–D to be made. Since A and B are the more conventional assumptions, the surface conductivity equations for these cases will be developed.

The equation for the Stern layer is:[5]

$$K_0\,(\epsilon - \zeta) = FZ\left\{\frac{1}{1 + \dfrac{1}{18c}\,e^{\frac{\Phi_+ - F\zeta}{RT}}} - \frac{1}{1 + \dfrac{1}{18c}\,e^{\frac{\Phi_- + F\zeta}{RT}}}\right\} + \sqrt{\frac{DRT}{2\pi}}\,c\left\{e^{\frac{F\zeta}{2RT}} - e^{\frac{-F\zeta}{2RT}}\right\} \tag{1}$$

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[5] Symbols used:

a = area of glass particles enclosing 1 cm³. of $5 \times 10^{-4}\,M$ potassium chloride.

$A = \dfrac{e^{\frac{F\zeta}{2RT}} + 1}{e^{\frac{F\zeta}{2RT}} - 1}$.

c = concentration in moles per cm³.

c_{I} = $5 \text{ x } 10^{-7}$ moles per cm³.

c_{II} = 3×10^{-6} moles per cm³.

c_{III} = 1×10^{-5} moles per cm³.

D = dielectric constant.

D^* = dielectric constant in Helmholtz layer.

F = Faraday (96,500 coulombs).

K_0 = capacity of Helmholtz layer.

l_a = mobility of anion.

l_c = mobility of cation.

R = gas constant (8.324×10^7 ergs).

T = absolute temperature.

u = electrosmotic velocity (cm. per second).

u_0 = electrosmotic velocity between Helmholtz and diffuse layer.

u_m = electrosmotic velocity in center of slit of thickness l.

u_h = electrosmotic velocity of outer Helmholtz layer.

u_h^* = u_hF, when E (electrical field) = 1.

z = number of ions per cm². of outer Helmholtz layer.

Z = moles of ions per cm². of outer Helmholtz layer.

$\alpha = \dfrac{2F\sqrt{2\pi c}}{\sqrt{DRT}}$.

δ = thickness of Helmholtz layer (5×10^{-8} cm. assumed).

ϵ = potential drop across entire double layer.

ζ = potential drop across diffuse layer.

η = viscosity coefficient.

Φ_+ = adsorption potential of cation.

Φ_- = adsorption potential of anion.

It follows from the equation that the outer Helmholtz layer contains

$$\frac{Z}{1 + \frac{1}{18c}\, e^{\frac{\Phi_+ - F\zeta}{RT}}} = \text{moles of cations per cm.}^2 \text{ of surface} \tag{2}$$

and

$$\frac{Z}{1 + \frac{1}{18c}\, e^{\frac{\Phi_- + F\zeta}{RT}}} = \text{moles of anions per cm.}^2 \text{ of surface} \tag{3}$$

Equations 2 and 3 may be simplified; the wall is assumed to be negatively charged.

$$18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} = \text{moles of cations per cm.}^2 \text{ of surface} \tag{2a}$$

and

$$18cZe^{\frac{-\Phi_- - F\zeta}{RT}} = \text{moles of anions per cm.}^2 \text{ of surface} \tag{3a}$$

The concentration of cations and anions in the diffuse layer is:

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \text{ moles of cations per cm.}^2 \text{ in excess of those normally present.} \tag{4}$$

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \text{ moles of anions per cm.}^2 \text{ in excess of those normally present.} \tag{5}$$

Since the Stern layer consists of a diffuse (Gouy) layer and a Helmholtz layer, we can use, for the value of the conductivity of the former (uni-univalent salts), the sum of Bikerman's (1) equations 19 and 23. It is:

Specific surface conductivity of diffuse layer (with electrosmose) =

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \left\{ l_c + \frac{DRT}{2\pi\eta} \right\} + \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \left\{ l_a + \frac{DRT}{2\pi\eta} \right\} \tag{6}$$

The specific surface conductivity expressed in equation 6 is based on the assumption that, at the boundary of the diffuse layer near the wall ($x = 0$), the electrosmotic velocity $u = 0$. This is not the case for the Stern layer, for we have, at the boundary of the diffuse layer ($x = 0$):

$$u = u_h = \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \tag{7}$$

This is the velocity of the outer Helmholtz layer. This means that integration of Bikerman's[6] equation 10 now involves the boundary conditions

$$\frac{\mathrm{d}u}{\mathrm{d}x} = 0 \tag{8}$$

when $x = \frac{l}{2}$, where the thickness of the Helmholtz layer is neglected;

$$u_h = \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \tag{9}$$

when $x = 0$. Performing the integration, Bikerman's equation 12 now becomes (see footnote 7)

$$u_m = \frac{E \cdot D \cdot \zeta}{4\pi\eta} + \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \tag{9}$$

The increase in conductivity (Δ_h) of the diffuse layer, caused by the movement of the outer Helmholtz layer, is

$$\Delta_h = \sqrt{\frac{DRT}{2\pi}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} u_h - \sqrt{\frac{DRT}{2\pi}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} u_h \tag{10}$$

When the potential ($\epsilon - \zeta$) in equation 7 is expressed in terms of charge (equations 2a and 3a, multiplied by F) and capacity of the Helmholtz condenser, we get

$$u_h = \frac{E \cdot \delta \cdot 18cZF \left\{ e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right\}}{\eta} \tag{11}$$

The conductivity of the diffuse (Gouy) layer is the sum of equations 6 and 10; or, substituting equation 11 in equation 10,

[6] $$E \cdot 8Fc \frac{Ae^{\alpha x} (A^2 e^{2\alpha x} + 1)\, \mathrm{d}x}{(A^2 e^{2\alpha x} - 1)^2} = \eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} \mathrm{d}x .$$

The left-hand side represents the electrical force causing osmosis which is exerted on a volume of solution of $1 \times 1 \times \mathrm{d}x$ cm^3. The right-hand side is the frictional force counterbalancing the electrical force.

[7] From equation 9 the important conclusion follows that electrosmose may still occur when $\zeta = 0$, since the Helmholtz layer still exists. See Monaghan, White, and Urban: J. Phys. Chem., May, 1935.

Specific surface conductivity of diffuse (Gouy) part of Stern layer (with electrosmose)

$$= \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \left\{ l_c + \frac{DRT}{2\pi\eta} + \frac{F^2 \cdot \delta \cdot 18cZ \left(e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right)}{\eta} \right\}$$

$$+ \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \left\{ l_a + \frac{DRT}{2\pi\eta} - \frac{F^2 \cdot \delta \cdot 18cZ \left(e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right)}{\eta} \right\} \quad (12)$$

The conductivity of the outer Helmholtz layer has to be added to the diffuse layer conductivity expressed in equation 12. The former is composed of two parts: the conductivity of the outer Helmholtz layer ions; the excess conductivity shown by these ions because the liquid moves. The total conductivity will be equal to:

$$\left\{ \begin{matrix} \text{Moles of cations in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} \times l_c + \left\{ \begin{matrix} \text{Moles of anions in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} \times l_a$$

$$+ \left\{ \begin{matrix} \text{Moles of cations in outer} \\ \text{Helmholtz layer} \end{matrix} - \begin{matrix} \text{Moles of anions in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} u_h^* \quad (13)$$

$u_h^* = \frac{u_h F}{E}$, where E is the applied potential.

Substituting from equations 2a, 3a, and 11:

Specific surface conductivity of outer Helmholtz layer (with electrosmose) =

$$18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} \cdot l_c + 18cZe^{\frac{-\Phi_- - F\zeta}{RT}} l_a + \frac{F^2\delta}{\eta} \left\{ 18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} - 18cZe^{\frac{-\Phi_- - F\zeta}{RT}} \right\}^2 \quad (14)$$

The specific surface conductivity of the entire (Stern) double layer is the sum of equations 12 and 14.

When no electrosmose occurs (high frequency A.C.), the specific surface conductivity becomes:

Specific surface conductivity (no electrosmose)

$$= \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ \left(e^{\frac{F\zeta}{2RT}} - 1 \right) l_c + \left(e^{\frac{-F\zeta}{2RT}} - 1 \right) l_a \right\}$$

$$+ 18cZ \left\{ e^{\frac{-\Phi_+ + F\zeta}{RT}} l_c + e^{\frac{-\Phi_- - F\zeta}{RT}} l_a \right\} \quad (15)$$

EXPERIMENTAL

The surface conductivity was determined in the following manner. Pyrex glass particles were equilibrated with potassium chloride and sodium chloride solutions (1.25 × 10^{-4} M to 1 × 10^{-1} M), transferred to a conductivity cell, and the conductivity as well as the *volume* of the particles carefully determined. After deducting bulk from observed conductivity, the difference represented the total surface conductivity. The surface area of the glass particles being known,[8] the specific surface conductivity (conductivity per cm.^{2}) is also known.

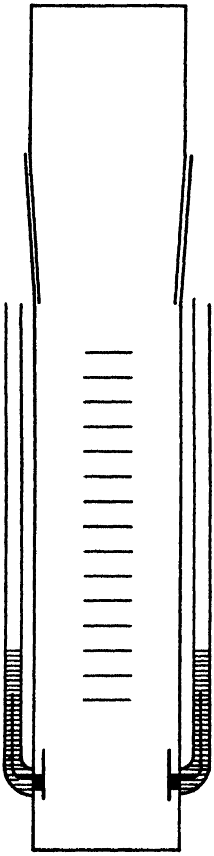

FIG. 1

The experimental determination of specific surface conductivities will now be discussed.

1. *Apparatus*

The measurements were carried out in a kerosene bath (9) at 25.000° ± 0.002°C. The conductivity cell was constructed of Pyrex glass and had a ground glass joint stopper (figure 1). It was graduated and carefully calibrated. The Wheatstone bridge was a 5-dial Gray instrument, coils accurate to 0.025 per cent. The current was supplied by a Leeds and Northrup 1000-cycle motor generator. The cathetometer used read to 0.02 mm.; 0.01 mm. could be estimated.[9] This permitted the volume of the Pyrex glass particles (52–55 cc.) to be read to ± 0.005 cc. The volume readings were taken with the conductivity cell in the constant temperature bath. The salts used were Kahlbaum's "Zur Analyse" grade. The interferometer was a Zeiss instrument.

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[8] See section 10, below.

The need for careful measurements is obvious, as surface conductivity is obtained by subtracting bulk conductivity from observed conductivity. Dividing total surface conductivity by the area of the glass particles gives the conductivity per cm.^{2} of surface. As was pointed out previously, the micro surface structure should not affect this calculation.

2. Volume occupied by constant amount of Pyrex glass particles as a function of electrolyte concentration

We early noticed that a given amount of Pyrex glass particles does not occupy the same volume in solutions of different electrolyte concentration.[10] This phenomenon had already been observed by Wo. Ostwald and von Buzagh (5, 11, 16). The latter observed a volume change of as high as 55 per cent, when quartz particles were transferred from water to benzene. Neglect of this factor may lead to serious errors in surface conductivity measurements.[11]

3. Effect of the amount of Pyrex glass particles in the cell on the cell constant

When a small amount of Pyrex glass particles is used, such that the electrodes are just covered by the particles, a value for the cell constant is obtained which is less than the one found when more particles are placed in the cell. In both cases the remainder of the cell volume is filled with solution to the same mark. As more and more particles are added, the differences in cell constant grow less. Finally a region is reached where the cell constant is unaffected by further addition of glass particles. The measurements must be performed with amounts of glass particles which lie in this region. Otherwise the volume changes discussed in section 2 will bring about unknown changes in the cell constant.

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[9] We are indebted to Prof. A. L. Hughes for the loan of this instrument.

[10] The effect of vibration on sedimentation volume must not be confused with the above effect.

[11] Fairbrother and Balkin (J. Chem. Soc. 1931, Part I, 1564–78) obtained their cell constant in aqueous 0.1 *M* potassium chloride and applied this value to measurements in benzene solutions. They make no mention of a volume correction.

4. *The size of the Pyrex glass particles and its influence on the reliability of the measurements*

The particles were obtained by grinding Pyrex chemical glassware in a mortar and sieving. The fraction between 100 and 200 mesh was retained, weighed, washed one hundred times with boiling distilled water, equilibrated with potassium chloride solution, and transferred to the conductivity cell.

Under these conditions it was difficult to duplicate our readings. Some improvement was noted after the cell and contents had been shaken vigorously and after the powder had settled spontaneously in the thermostat. But as the powder surface was still cloudy and uneven, the volume measurements were of doubtful value. Finally the difficulty was overcome by using only the particles which settled within 1 minute. This powder gave sharply defined horizontal surfaces and reproducible volume and conductivity measurements, as shown by a representative experiment (table 1). The estimate of the area of all the glass powder, based on microscopic observation of about two hundred particles, is 20,000 cm². This value is probably too low, as no correction for surface curvature was applied. The area determined by surface conductance is 27,000 cm².

TABLE 1

Constancy of sedimentation volumes and resistance

SOLUTION	VOLUME	RESISTANCE
	cc.	*ohms*
1.25×10^{-4} *M* KCl	52.06_7	$8\ 975 \times 10^4$
	$51\ 97_4$	$9\ 055 \times 10^4$
	$51\ 92_3$	$9\ 075 \times 10^4$
	$51\ 92_5$	9.044×10^4
	$52\ 09_5$	9.024×10^4
$1 \quad \times 10^{-2}$ *M* KCl	51.82_9	1408.9
	$51\ 85_3$	1406 5
	51.84_7	1409.8
	$51\ 94_1$	1406.4
	51.89_3	1405.0
	$51\ 81_6$	1409.2
	51.80_9	1409.0

5. *Change in cell constant (Parker effect)*[12]

The Parker effect of a conductivity cell comprises a set of factors, such as construction of the cell, bridge set-up, etc., which result in a variation of cell constant with concentration. The effect was evaluated from conductivity measurements in 2.5×10^{-4}, 1×10^{-3}, 3×10^{-3}, 3×10^{-2}, 7×10^{-2}, 9×10^{-2}, 1×10^{-1}, and 2.5×10^{-1} *M* potassium chloride. The values for the specific conductivity of these solutions were taken from a paper by Shedlovsky (13).[13] The observed resistances of these solutions in our cell covered the range 56–44,000 ohms. The cell constant is expressed by the empirical equation

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[12] G. Jones and G. M. Bollinger (J. Am. Chem. Soc. **53**, 411 (1931) made a careful study of this effect. All references will be found in their paper.

$$\text{Cell constant} = 0.6970 - 0.00265 \log R$$

from which the percentage change of the cell constant at two different resistances can be calculated. The equation holds to about 60 ohms. Below this value, polarization of the electrodes begins to exert an influence on cell constants.

It should be shown next that the percentage change of the constant with resistance is uninfluenced by the presence of glass particles between the electrodes. On account of surface conductivity, cell constants cannot be calculated from conductivity measurements, except in concentrated solutions.

Hence the following procedure was adopted. The glass particles and solution were placed inside of a sealed, flat-bottomed glass tube which was coaxially cemented inside the conductivity cell. The annular space between the conductivity cell wall and the glass tube was then filled with a series of known solutions and their conductivities determined. The percentage variation of the cell constant was found to be the same as before.

6. *Equilibration of electrodes*

It is known that platinized platinum electrodes may retain adsorbed electrolyte with great tenacity (2). The effect is particularly noticeable when dilute solutions are placed in cells previously containing concentrated solutions. The electrodes were carefully equilibrated with the solution before conductivity measurements were taken.

7. *Equilibration of Pyrex glass particles*

The particles were freed from electrolyte by repeated washing with boiling distilled water each time, before being equilibrated with a given electrolyte solution. The latter was decanted and renewed until the conductivity of the supernatant liquid or its refractive index (interferometer) was the same as that of the solution taken from the volumetric glass-stoppered Pyrex flask. A rubber bulb was used for operating a wash bottle, thus preventing contamination by exhaled carbon dioxide.

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[13] For a discussion of Shedlovsky's values see G. Jones and B. C. Bradshaw (J. Am. Chem. Soc. **55**, 1780 (1933)). We are indebted to Prof. Grinnell Jones for a résumé of specific conductivity measurements (private communication).

8. Conductivity of the water

The latter was always determined and the surface conductivity measurements of the powder were corrected accordingly. This is important in dilute solutions, such as 1.25×10^{-4} *M* potassium chloride, where the specific conductivity of the water amounted to 8 per cent of the specific conductivity of the solution.

9. Determination of the density of the Pyrex glass particles

The density was calculated from the volume increase in our cell, when a known weight of powder was added to a known volume of water. We found $d_{4°}^{25°} = 2.225 \pm 0.005$.

10. Determination of effective surface area of Pyrex particles

The effective surface area of the particles which are *in contact with 1 cm.*^{3} *of solution* was calculated according to the expression:

$$\frac{\text{Cell constant}}{\text{Observed resistance}} = \text{bulk specific conductivity} + \text{effective surface area (cm.}^2) \times \text{specific surface conductivity} \quad (16)$$

In this equation all quantities, except the area, are known for 5×10^{-4} *M* potassium chloride, the specific surface conductivity being 4.3×10^{-9} mho, which is the value obtained with slits of known dimensions using A.C.[14] The effective surface area may be defined as the area of that portion of the surface in contact with 1 cm.^{3} of solution (interstitial liquid) which contributes to conductance.

11. Change of cell constant with concentration

The cell constant of the conductivity cell containing the glass powder is calculated from the observed conductivity in 1×10^{-1} *M* potassium chloride. The bulk conductance is so great in this solution that the contribution of the surface may be neglected. At all other concentrations, the cell constant is found by applying the percentage correction outlined under section 5.

12. Correction of cell constant when the glass powder volume changes

It has been tacitly assumed so far that a given quantity of glass powder, when settling spontaneously, will always occupy the same volume, irrespective of the nature and concentration of the solution in which the powder is suspended. This is not the case (see section 2).

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[14] See Urban, Feldman, and White (J. Phys. Chem., April, 1935). The older figure of 2.24×10^{-9} mho, obtained by White, Urban, and Van Atta (J. Phys. Chem. **36**, 1371 (1932)) does not apply in this calculation, owing to the operation of Bikerman's membrane potential factor, discussed by Urban, Feldman, and White, and of electrosmose.

For instance, the volume of glass powder + solution was 51.759 cc. in 5×10^{-4} M potassium chloride, but 53.482 cc. in 1×10^{-1} M potassium chloride (see column 2, table 3a).

In order to carry out the calculations outlined under sections 10 and 11, it is necessary to determine what the cell resistance in 1×10^{-1} M potassium chloride would have been if the volumes of the glass particles + solution had been 51.759 cc. (instead of the observed 53.482).

The correction has been made by equation 17

$$\frac{R}{r} = \frac{(V_r - g)}{(V - g)} \tag{17}$$

where R = calculated resistance at volume V (glass powder + interstitial liquid),

r = observed resistance at volume V_r,

g = volume of glass particles (weight ÷ density).

Equation 17 can be tested. Thus we found that 24.79 cc. of particles suspended in 0.1 M potassium chloride solution gave a V_r reading of 54.28 cc. in one determination, and 53.48 in another, probably due to vibration. The corresponding (observed) resistances were 146.44 and 150.49, respectively. The resistance at the larger volume, calculated from the resistance at the smaller volume, is 146.48 ohms (observed 146.44 ohms).

The factor of non-homogeneous packing does not enter into the surface conductivity measurements, because the particles were always allowed to settle spontaneously. After one determination, the cells were shaken and both volume and resistance were redetermined. This was repeated from five to ten times. The volume and resistance measurements agreed closely, indicating that the same kind of packing always occurred under our experimental conditions.

DISCUSSION

Calculations

The observed specific surface conductivities (tables 3a, 3b, column 14) were next compared with the ones calculated according to equations 12 + 14, and 15, respectively, after appropriate values for ζ and the constants had been substituted.

The ζ-potentials were those of Lachs and Biczyk (10), calculated from their experimentally determined stream potentials. The following values were obtained (table 2). Since Lachs and Biczyk gave the stream potentials only for 1×10^{-4}, 1×10^{-3}, and 1×10^{-2} M potassium chloride, it was necessary to interpolate. When the log of the potassium chloride concentration is plotted against the log of the stream potential, a nearly straight line is obtained. The interpolated ζ-potentials may, therefore, be considered as reasonably accurate. The interpolated Lachs and Biczyk ζ value for 5×10^{-4} *M* potassium chloride is 0.1209 volt; our (experimental) value is 0.1214 volt (17). The adsorption potentials, Φ_+ and Φ_-,[15] have also been treated as constant and independent of the concentration. This seems permissible in the present concentration range.

The values for $Ze^{\frac{-\Phi_+}{RT}}$ and $Ze^{\frac{-\Phi_-}{RT}}$ were determined by solving two simultaneous equations, obtained by substituting ζ and specific surface conductivity (the experimental value) for the two concentrations 3×10^{-3} *M* and 1×10^{-2} *M* potassium chloride, in equations 12 + 14 (assumption A, electrosmose), and in equation 15 (assumption B, no electrosmose). These two solutions possess a Helmholtz layer conductance which is high compared with that of the diffuse layer. For this reason the uncertainty in the value of the (calculated) diffuse layer conductivity cannot greatly affect the fraction of the observed surface conductivity which is assigned to the Helmholtz layer.[16] A tentative value (η × 1.2) was used for the vis-

TABLE 2

Values of ζ-potential at various concentrations

CONCENTRATION OF POTASSIUM CHLORIDE SOLUTION	ζ-POTENTIAL
M	*volts*
1.25×10^{-4}	0.1100
2.5×10^{-4}	0.1160
5×10^{-4}	0.1209
1×10^{-3}	0.1226
3×10^{-3}	0.1113
1×10^{-2}	0.0816

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[15] Φ_+ and Φ_- signify adsorption "potentials" in the outer Helmholtz layer. They are of the same kind as those encountered near crystal surfaces. W. H. Zachariasen (J. Am. Chem Soc. **54**, 3841–51 (1932)) has recently developed a picture of the atomic arrangement in oxide glasses. He finds that atoms in glasses are linked together by forces essentially as in crystals. There are extended three-dimensional networks. The principal difference between crystal and glass networks is symmetry and periodicity in the crystal and their absence in the glass network. In this connection, the discussion of surface forces by Irving Langmuir (J. Am. Chem. Soc. **40**, 1361 (1918)) is of interest. It may be further pointed out that the ζ-potential at fused and unfused glass surfaces is the same. See Monaghan and White (J. Phys. Chem., in press).

[16] Solution of these simultaneous equations (KCl):

	$z = 1 \times 10^{15}$	$z = 1.27 \times 10^{15}$
A (electrosmose)	$\Phi_- = -2.5 \times 10^{11}$	-2.4×10^{11}
	$\Phi_+ = -8.0 \times 10^{10}$	-6.1×10^{10}
B (no electrosmose)	$\Phi_- = -2.5 \times 10^{11}$	-2.5×10^{11}
	$\Phi_+ = -6.9 \times 10^{10}$	-7.4×10^{10}

Solution of the two simultaneous equations (NaCl):

cosity coefficient of the Helmholtz double layer. The correction was made according to the H. A. Lorentz equation, cited by Bikerman. A similar correction has been developed by The Svedberg and Hugo Anderson (15).

Sedimentation volume

The regular decrease of the values for the interstitial solution (table 3a, column 4) indicates a closer approach of the particles with increasing electrolyte concentration. The interpretation of this phenomenon by Zocher (18) is this: "Beim Entladen durch Elektrolyte nimmt der Abstand zwischen den Schichten ab. . . . ." We do not believe that this shrinkage depends on ζ-potential changes alone. If the volume decrease effect were associated only with ζ-potentials, the two should run parallel, which is not the case.[17] The effective particle volume falls progressively beginning with 1.25×10^{-4} *M* potassium chloride, until a second effect appears which again causes a rise in sedimentation volume. The ζ-potentials, however, do not decrease progressively, but go through a maximum.

The sharp rise in sedimentation volume beginning between 3×10^{-3} *M* and 1×10^{-2} *M* potassium chloride is probably not due to a "Haftefekt" (4), since the glass particles were far from dehydrated, as evidenced by the fact that in 4.5×10^{-4} *M* thorium chloride solution the volume of interstitial solution is about 2 cc. less than in 3×10^{-3} *M* potassium chlo-

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(no electrosmose) $\Phi_- = -2.6 \times 10^{11}$ -2.5×10^{11}
$\Phi_+ = -8.1 \times 10^{10}$ -7.5×10^{10}

Solving for $Ze^{\frac{-\Phi_+}{RT}}$ and $Ze^{\frac{-\Phi_+}{RT}}$, instead of for Φ_+ and Φ_-, offers the advantage that Z does not have to be evaluated separately.

The ratio $Ze^{\frac{-\Phi^+}{RT}} \Big/ Ze^{\frac{-\Phi_-}{RT}}$ corresponds to the ratio of anions to cations in the outer Helmholtz layer, *in the absence* of a double layer electrical field, i.e., if van der Waals forces alone were operative (E. Hueckel, reference 8, p. 57). For potassium chloride, it is 0.001, i.e., for 10,000 Cl^- there are 10 K^+ in the outer Helmholtz layer.

For the time being only approximate values can be assigned to Z. Stern uses the value $\frac{1 \times 10^{15}}{6.06 \times 10^{23}}$. Since the glass particles are hydrated, Z can be approximately calculated by using Tammann's (Z. anorg. Chem. **158**, 1 (1926)) value of 0.992 for the specific volume of depolymerized water. The number of water molecules per cm^3. is $\frac{6.06 \times 10^{23}}{0.992 \times 18} = 3.4 \times 10^{22}$. The approximate number of lattice points z is $\sqrt[3]{3.4 \times 10^{22}} = 1 \times 10^{15}$, compared with a value of 1.27×10^{15} for the number of lattice points per cm^2. in a potassium chloride crystal.

[17] It may be concluded that the electroviscous effect must be due to more than one factor, in agreement with Bungenberg de Jong, Kruyt and Lens (Kolloidchem. Beihefte **37**, 395 (1933)).

TABLE 3a

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
KCl MOLES PER LITER OF SOLUTION	TOTAL VOLUME GLASS + SOLUTION	VOLUME OF GLASS PARTICLES	VOLUME OF SOLUTION (INTERSTITIAL)	OBSERVED RESISTANCE	CALCULATED RESISTANCE OF 0 1 *M* KCl	CELL CONSTANT (THEORETICAL)	CELL CONSTANT CORRECTED FOR PARKER EFFECT (ACTUAL)	CONDUCTIVITY PER CM ³ OF SOLUTION	SPECIFIC CONDUCTIVITY OF KCl (SHEDLOVSKY)	SPECIFIC CONDUCTIVITY OF H_2O	SURFACE CONDUCTIVITY PER CM.³	EFFECTIVE SURFACE AREA IN CM ² PER CM.³ OF SOLUTION	SURFACE CONDUCTIVITY PER CM ²	$l_c = l_a$
moles	cc	cc.	cc.	*ohms*	*ohms*			*mhos* × 10^{-5}	× 10^{-5}	× 10^{-5}	× 10^{-6}		× 10^{-9}	
1.25 × 10^{-4}	52 00$_0$	24.79	27.21	90350	158 68	2 045$_6$	2 024$_0$	2 24$_{02}$	1 860	0.151	2.29	1058	2 17	74 40
2.5 × 10^{-4}	51.87$_3$	24 79	27 08	47840	159 44	2 055$_4$	2 036$_0$	4 25$_{59}$	3 709	0 151	3.96	1063	3 73	74 20
5 × 10^{-4}	51.75$_9$	24 79	26 97	25575	160 09	2 063$_7$	2 046$_0$	8 00$_{02}$	7 390	0 151	4 59	1067	4 30	73 90
1 × 10^{-3}	51.67$_3$	24.79	26 88	13147	160.62	2.070$_6$	2 055$_6$	15 6$_{35}$	14 693	0 151	7 91	1071	7 39	73 47
3 × 10^{-3}	51 54$_6$	24 79	26 76	4558	161 34	2 079$_9$	2.068$_4$	45 3$_{51}$	43 485	0.151	17 45	1075	16 23	72 48
1 × 10^{-2}	51 85$_4$	24 79	27 06	1407	159.55	2 056$_9$	2 047$_4$	145.$_{43}$	141.32	0.151	39 6	1063	37 20	70 66
1 × 10^{-1}	53 48$_2$	24 79	28 69	150 4$_9$		1 940$_0$	1 940$_5$	1289	1289	0 151				

TABLE 3b

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
NaCl MOLES PER LITER OF SOLUTION	TOTAL VOLUME GLASS + SOLUTION	VOLUME OF GLASS PARTICLES	VOLUME OF SOLUTION (INTERSTITIAL)	OBSERVED RESISTANCE	CALCULATED RESISTANCE OF 0.1 *M* NaCl	CELL CONSTANT (THEORETICAL)	CELL CONSTANT CORRECTED FOR PARKER EFFECT (ACTUAL)	CONDUCTIVITY PER CM.^{3} OF SOLUTION	SPECIFIC CONDUCTIVITY OF NaCl (SHEDLOVSKY)	SPECIFIC CONDUCTIVITY OF H_2O	SURFACE CONDUCTIVITY PER CM.^{2}	EFFECTIVE SURFACE AREA IN CM.^{2} PER CM.^{3} OF SOLUTION	SURFACE CONDUCTIVITY PER CM.^{2}	l_c	l_a
moles	*cc.*	*cc.*	*cc.*	*ohms*	*ohms*			*mhos* $\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-6}$		$\times 10^{-9}$		
1.25×10^{-4}	52.35_8	24.79	27.57	99850	189.25	2.018_9	1.997_0	2.00_0	1.569	0.191	2.24	1044	2.15	50.21	75.31
2.5×10^{-4}	52.28_0	24.79	27.49	55470	189.80	2.024_8	2.004_9	3.61_4	3.127	0.191	2.96	1047	2.83	50.03	75.05
5×10^{-4}	52.06_7	24.79	27.28	29900	191.27	2.040_5	2.022_5	6.76_4	6.225	0.191	3.48	1055	3.30	49.80	74.70
1×10^{-3}	51.81_3	24.79	27.02	15504	193.10	2.060_0	2.044_2	13.18_5	12.372	0.191	6.22	1065	5.84	49.49	74.23
3×10^{-3}	51.66_5	24.79	26.88	5389	194.11	2.070_8	$2\ 058_8$	38.20_4	36.558	0.191	15.55	1071	14.53	48.74	73.12
1×10^{-2}	51.61_6	24.79	26.83	1686	194.47	2.074_6	2.066_8	122.5_6	118.43	0.191	39.4	1073	36.74	47.37	71.06
1×10^{-1}	53.02_0	24.79	28.23	184.8_3	184.83	1.971_7	1.971_7	$1067._0$	1066.8	0.191					

ride. The cause for this rise demands further investigation. It may possibly be connected with a rigidity change of the lyosphere which accompanies the increase in double layer field strength. This has shrunk to a thickness of 2×10^{-7} cm. in 1×10^{-1} M potassium chloride, compared with a thickness of 55×10^{-7} in 1.25×10^{-4} M potassium chloride (see below). For purposes of the work presented here, an exact knowledge of the mechanism producing these changes is not necessary.

The conductivity of the diffuse layer (for potassium chloride $l_a = l_c$) without electrosmose is, per cm.^{2} of surface,

$$\sqrt{\frac{DRTc}{2\pi F^2}}\left\{e^{\frac{F\zeta}{2RT}} + e^{\frac{-F\zeta}{2RT}} - 2\right\}l_c$$

This is the difference between total diffuse layer ions, and the ions normally present. The latter quantity is

$$\sqrt{\frac{DRTc}{2\pi F^2}} \cdot \text{moles of solute}$$

Inasmuch as 1 cm.^{3} contains normally c moles, the thickness of the diffuse double layer must be

$$\sqrt{\frac{DRTc}{2\pi F^2}} \Big/ c = \sqrt{\frac{DRT}{2\pi F^2 c}} \text{ cm.}$$

The following thicknesses have been calculated (table 4).

Accuracy of measurements

The observed specific surface conductivities in 3.0×10^{-3} M potassium chloride and 1.0×10^{-2} M potassium chloride are believed accurate to ±10 per cent. This percentage error is deduced as follows. The accuracy of the values in table 3a, column 9, is ±0.2 per cent; in column 10, ±0.02 per cent. The error in column 12 (total observed surface conductivity in 1 cm.^{3} of solution) depends on how small a fraction of column 9 it is. If total surface conductivity is one-tenth of total specific conductivity, the error is ±2 per cent; if it is one one-hundredth, the error is ±20 per cent. In calculating specific surface conductivity, column 14, the effective surface area of the powder must be known. It is obtained by dividing total surface conductivity in 5.0×10^{-4} M potassium chloride by 4.3×10^{-9}. If $\pm\, a$ is the error in total surface conductivity A, and $\pm b$ the error in the specific surface conductivity B, then the error in the area will be

$$\pm\,\frac{\sqrt{B^2a^2 + A^2b^2}}{B^2} \qquad (18)$$

On the basis of an error of ±3.5 per cent in total surface conductivity and ±7.5 per cent in the specific surface conductivity in 5.0×10^{-4} *M* potassium chloride, the error in the area is ± 8 per cent. The percentage error for all values in table 3, column 14, has been estimated by the above equation of Fenner (3). It is about ±10 per cent. It follows that the accuracy of the calculated $Ze^{\frac{-\Phi}{RT}}$ values, allowing furthermore for the uncertainty in δ, the thickness of the Helmholtz layer, l = ionic mobility (assumed to be normal), and the value of ζ, must be of the order of ±20 per cent.

TABLE 4

Thickness of diffuse double layer in various potassium chloride solutions

MOLES KCl PER LITER	THICKNESS OF DIFFUSE LAYER
moles	*cm.*
1.25×10^{-4}	5.5×10^{-6}
2.5×10^{-4}	3.9×10^{-6}
5×10^{-4}	2.7×10^{-6}
1×10^{-3}	1.9×10^{-6}
3×10^{-3}	1.1×10^{-6}
1×10^{-2}	0.6×10^{-6}
1×10^{-1}	0.2×10^{-6}

TABLE 5

MOLES OF SALT PER LITER	OBSERVED SPECIFIC SURFACE CONDUCTIVITY	CALCULATED ACCORDING TO 12 + 14 (ELECTROSMOSE)	CALCULATED ACCORDING TO GOUY'S DOUBLE LAYER (1)	CALCULATED ACCORDING TO 15 (NO ELECTROSMOSE)	CALCULATED ACCORDING TO GOUY'S DOUBLE LAYER (1)
	mhos $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$
KCl					
1.25×10^{-4}	2.17	0.93	0.51	0.94	0.34
2.5×10^{-4}	3.73	1.85	0.84	1.97	0.56
5.0×10^{-4}	4.30	4.18	1.36	4.36	0.91
1.0×10^{-3}	7.39	8.52	2.03	8.61	1.35
3.0×10^{-3}	16.23	(16.23)	2.58	(16.23)	1.72
1.0×10^{-2}	37.20	(37.20)	2.13	(37.20)	1.42
NaCl					
1.25×10^{-4}	2.15			0.80	0.27
2.5×10^{-4}	2.83			1.72	0.44
5.0×10^{-4}	3.30			3.89	0.72
1.0×10^{-3}	5.84			7.77	1.06
3.0×10^{-3}	14.53			(14.53)	1.36
1.0×10^{-2}	36.74			(36.74)	1.13

The error in the volume occupied by the glass particles practically cancels out in the division described in section 12.

RESULTS

The experimental data have been summarized in tables 3a and 3b, which are self-explanatory.

In table 5 observed and calculated specific surface conductivities have been tabulated for potassium chloride and sodium chloride.[18] The agreement between observed and calculated values is good, when the sources of error and the experimental difficulties are kept in mind.

The values calculated according to Bikerman's equations 19 and 26 have also been included. It is seen that they are far too low.

We interpret these results as confirming the essential accuracy of the Stern double layer theory which has been tested here for the first time.

SUMMARY

1. Specific surface conductivities of Pyrex glass particles in potassium chloride and sodium chloride solutions of concentration 1.25×10^{-4} *M* to 1×10^{-2} *M* were determined.

2. The surface conductivities represent the same fraction of total conductivity as in a glass capillary of about 10μ diameter.

3. An equation, based on the Stern double layer, for calculating specific surface conductivities was developed.

4. The calculated values are in agreement with experiment; values calculated according to Gouy's theory are not.

5. Evidence is adduced to show that (a) electrosmose may occur when $\zeta = 0$; (b) a sudden increase in sedimentation volume need not be due to "Hafteffekt"; (c) the electroviscous factor contains more than one component.

6. The thickness of the diffuse layer has been calculated.

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[18] It has been assumed that ζ-potentials of sodium chloride solutions were the same as those of potassium chloride.

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THE MAGNITUDE OF SURFACE CONDUCTIVITY[1]

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The only measurements of surface conductivity on surfaces of approximately known area measured with alternating current are those carried out during a period of ten years at Bristol and Stanford Universities and finally published in 1929 (8, 9). They comprise measurements made with optically polished glass and with ordinary Pyrex tubing in contact with aqueous solutions of potassium chloride and, in addition, measurements of the surface conductivity of an insoluble film of stearic acid on water. All yielded results of the same magnitude, namely, several mhos × 10^{-8} when referred to 1 square centimeter of surface. Nevertheless, many writers have decided to reject these results for two reasons. In the first place, the conductivity is far larger than can be accounted for by current theories in which the phenomena are referred wholly to the outer portion of the diffuse part of the double layer. In the second place, the only other measurements from another laboratory (11) with approximately known area of surfaces in contact with solutions of potassium chloride have yielded little or no surface conductivity.

These other measurements by White, Urban, and collaborators are characterized by three important features. First, the measurements are made with direct current. Next, the liquid was kept in motion by applied hydrostatic pressure, streaming through the capillary. Lastly, almost alone amongst those who have measured the conductivity of salt solutions since the time of Kohlrausch, these authors have not seen fit to correct the observed conductivity of potassium chloride solutions for the conductivity of the solvent. This correction nullifies the very slight surface conductance which they report, rendering it zero or negative.

We have now repeated with every precaution measurements with alternating current on systems consisting of tubing in contact with solutions of potassium chloride, and we have also extended and developed the measurements of surface conductivity of films of stearic acid, oleic acid, and palmitic acid on water. The results substantially confirm the previous measurements with alternating current, which would now appear to be fully established and to require modification of any theory with which they are not in accord.

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[1] Presented before the Eleventh Colloid Symposium held at Madison, Wisconsin, June 14–16, 1934

We also emphasize what has been implicitly known but not fully realized or explicitly expressed except in papers from this laboratory (1, 6, 7), namely, the free mobility of the mobile ions of the double layer. In other words we stress the importance of the recognition of the fragility of the double layer. Attempts to measure electrokinetic properties of the double layer easily tend profoundly to modify or to destroy the object of measurement.

Mobile ions lie passive in the liquid which surrounds them and in the absence of an applied force have neither any definite tendency towards directed movement nor, apart from discontinuities in the nature of the surface, any tendency to resist being carried along when the liquid in which they are embedded is moved parallel to the double layer. Any streaming of the liquid therefore, whether produced by applied hydrostatic pressure or induced by the application of direct current as in electrosmosis, sweeps along with it the mobile ions of the double layer. These would have to be replaced if the double layer is not to remain depleted.

Surface conductance as measured can only be due to the physical presence of bodily carriers or ions free to move under the conditions of the experiment and in numbers greater than that corresponding to the ordinary bulk conductivity of the unchanged liquid or solution. If the mobile ions are being ejected from the outlet of the capillary system, the surface conductivity will disappear unless they are replaced. Only immobile ions are left upon the surface. The replacement has to occur in the stream of liquid at the inlet. Ordinary electrolysis cannot accomplish this, because it merely discharges a space charge without in any way altering the concentration of the intermediate liquid through which the current is carried, as is well known in the field of transport or migration measurements. Especially is this evident with potassium chloride where both ions move with equal velocity in opposite directions, so that electrolysis through the entering stream of liquid cannot affect the total number of ions present, since a gain of one ion is exactly compensated with a loss of another of opposite charge and equal conductivity. Hence any loss of ions in the effluent cannot be replenished by ordinary electrolysis in the inflowing liquid. The depletion must be made good by diffusion, which requires time. The time required may be too great when the liquid is moving with appreciable velocity.

Electrokinetic phenomena need not by any means disappear when, through streaming, the surface conductivity is thus partially or largely eliminated. Redistribution of the available charges within the capillary system in a direction perpendicular to the double layer will be almost instantaneous, and streaming potential or electrosmosis will remain prominent. Thus, even surface conductivity will be actually present, although practically masked by the corresponding depletion of the bulk solution available within the capillary.

An especially illuminating case for consideration is where there are no electrokinetic phenomena, either because the number of positive and negative points on the surface is equal, or because the surface is not charged anywhere but there is a general accumulation of ions in the neighborhood. In both cases there would be observable surface conductivity as long as the total number of ions in the solution exceeded that in the same volume of liquid outside the capillary system. Rapid flushing out with that liquid would sweep away the excess carriers and with it the observable surface conductivity.

It follows from the considerations outlined above that one should not expect exact concordance between electrokinetic effects measured by different procedures which directly modify the preëxisting double layer. The most striking instance of this is that observed by DuBois and Roberts (private communication) in one and the same system in which a ζ-potential was positive and equal to $+32$ millivolts as measured by streaming potential, but negative and equal to -47 millivolts as measured by electrosmosis. The measurements were made in immediate alternation without any other interference with the system.

Finally, it is possible that certain ions in the double layer may be capable of a restricted excursion and so may contribute to conductance as measured with alternating current, whilst not being measured by direct current. A careful examination of Ohm's law and comparison of the two kinds of current should determine this point.

EXPERIMENTAL METHODS[2]

Three experimental methods were employed, and in each case a whole series of cells was designed successively to eliminate difficulties of measurement or interpretation. The last cells actually used in each series were of Pyrex glass and are illustrated in figures 1, 2, and 3. Figure 1 represents a cell containing seven concentric tubes between platinum electrodes which fill the cross section of the cell and are plane polished on the surfaces facing the concentric tubes. They are sufficiently far apart to permit of the tubes being slid in and out of each other without quite coming apart.[3] The distance between electrodes was checked by measurement with a travelling microscope in each experiment. The tubes were settled by gravity on the plane surface; in every case a measurement was made before and after agitation, tapping, standing undisturbed, sliding the tubes in and out, etc. The tubes were originally cleaned with chromic acid solution, but were kept under constant changes of water or solution for periods of months. The final measurements were taken after a year of continuous

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[2] Experiments by J. F. F.

[3] The electrodes should not be much further apart than their own diameter, and the inner tubes replaced by a single solid cylinder. Then each would rest firmly upon its base without danger of tilting.

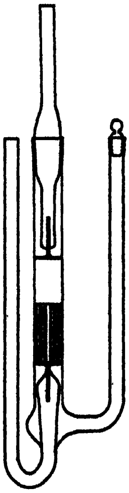

FIG. 1. CELL WITH CAPILLARY SPACES BETWEEN CONCENTRIC TUBES

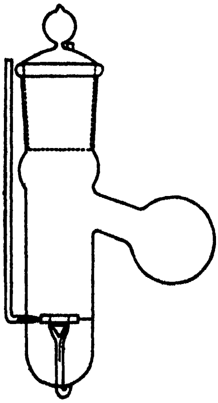

FIG. 2

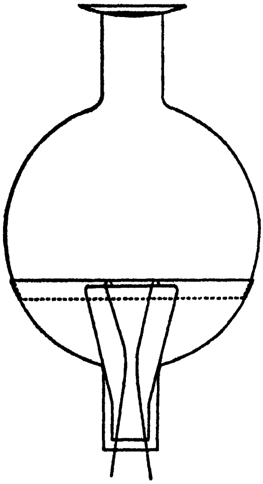

FIG. 3

FIG. 2. CELL FOR DETERMINING SURFACE CONDUCTIVITY OF THE AIR-WATER INTERFACE BY ELIMINATING THE EFFECT OF BULK CONDUCTIVITY

FIG. 3. CIRCULAR TROUGH FOR MEASURING INSTANTANEOUS PRODUCTION OF SURFACE CONDUCTIVITY

The cell is shown empty

use since the last cleaning with chromic acid solution.[4] Recleaning was effected by heating to 400–500°C. The cell in figure 2 was heated in a blast flame. That in figure 3 was likewise heated in a free flame and in a muffle furnace.

Figure 2 for insoluble or slightly soluble films on water is a modification of that used by Peaker. The cell is first measured full of conductivity water; then again, without opening, with the meniscus immediately above the electrodes but not touching them. The ratio gives the ratio of bulk conductivities for the two positions. Without moving the meniscus, the film is placed upon the surface and ample time is allowed for equilibrium. The additional conductivity consists of surface conductivity and additional bulk conductivity. The latter is determined by raising the meniscus to the top position, applying the ratio previously determined. The cell is opened only to introduce the surface film. Excess liquid is stored in the side arm. The two essential points are that neither the electrodes nor their supports should come into contact with the surface, which might cover them with an insulating film. This requires correct adjustment of the size and position of the side arm.

Figure 3 is for nearly instantaneous observations of the production of surface conductivity. Here again neither the electrodes nor their supports touch the surface. The diameter is at least 12 cm. to avoid alterations in level at the electrodes due to surface tension changes at the walls.

Measurements were in all cases made by the latest Leeds and Northrup equipment, the Grinnell Jones bridge. Any supplementary resistances used were Curtis wound coils. The oil thermostat was adjusted to 25.00° ± 0.005°C. Potassium chloride solutions were made up by weight by the method of Parker and Parker. The specific conductivity of the water was 0.4–0.5 $\times 10^{-6}$ mho. Kahlbaum's best stearic and palmitic acids were used, together with some specially pure fatty acids made by Dr. Lepovsky of the University of California. In all cases they were repeatedly extracted with conductivity water before use.

EXPERIMENTAL DATA WITH CONCENTRIC TUBES (FIGURE 1)

The value of observed resistance represents in the case of each concentration a mean of many separate determinations which agree very closely among themselves. The cell was emptied and refilled with fresh solution several times, and the tubes were slid back and forth between individual measurements. The cell was always placed accurately vertical in the oil thermostat. At the end of measurements on one concentration the tubes were removed and the cell constant measured or remeasured before proceeding to the next higher concentration. In each instance the measured resistance without tubes agreed with the resistance calculated from the dimensions of the cell within 0.1 per cent. Dimensions of cell and tubes were as follows: cross section of tubes, 0.959 sq. cm.; length of tubes, 2.94 cm.; cross section of cell, 1.246 sq. cm.; distance between electrodes, 5.450 cm.; "surface cross section," 18.50 cm. (sum of circumferences). Observed values of specific surface conductivities are high because the microscopic surface of the tubes is much larger than the apparent area. These results were confirmed with a complete series of measurements with the same set of tubes in an earlier design of cell which, however, did not allow as exact an evaluation of k_s because it was not truly cylindrical.

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[4] Compare the similar prolonged treatment described on p. 3299 of a previous communication (9).

Rapid streaming of the liquid through the tubes always caused a rise in resistance which continued usually to a point at which there was no surface conductivity, thus demonstrating the fragility of the double layer.

EXPERIMENTAL DATA ON INSOLUBLE FILMS IN CLOSED CELL (FIGURE 2)

This cell gives consistently reproducible results for surface conductivity of acid films on water. It was cleaned by heating in an oven at 450–500°C., then filled with conductivity water to the proper level, closed and placed in a thermostat at 25°C. to come to equilibrium. The cell was carefully levelled so that the tops of the electrodes were horizontal. In general the contents of the cell reached equilibrium with the enclosed atmosphere in about twenty-four hours, at which time it was possible to pour the water back and forth without changing the resistance of the cell by as much as 0.1 per cent. Two resistances were measured: (I) resistance of the cell with all the water in the main cell and the meniscus far above the tops of the electrodes, and (II) resistance of the cell with part of the water poured into the side bulb so that the surface of the liquid was just above the upper edges of the electrodes.[5] Care was taken so that no part of the electrodes or supports broke the surface.

After completion of the first two measurements, the cell was opened and the surface of the liquid in both the main cell and side bulb coated with the acid film. Again the cell was closed and allowed to stand for twenty-four hours to come into equilibrium with the surface film. Extreme precautions were observed to change neither the position of the cell nor the height of the meniscus during contamination.

With equilibrium reëstablished, two more resistances were measured: III, resistance of the cell with the meniscus unchanged since measurement II, but with the addition of the surface conductivity of the film and a certain bulk conductivity due to a slight solubility of the fatty acid, and IV, resistance of the cell with the meniscus again raised above the edges of the electrodes as in position I. Resistance IV is lower than resistance I because of the conductivity of the small amount of dissolved fatty acid, and also probably because of a certain amount of contamination from the atmosphere when the cell was opened.

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[5] No difference was observed in the ratio of resistances I and II using conductivity water and using $N/1000$ potassium chloride.

The total surface conductivity is deduced from resistance III by calculating from resistance IV and the ratio between II and I the value for bulk conductance only, and hence necessarily taking the difference as surface conductivity. This is then corrected to specific surface conductivity from the dimensions of the electrodes. For example, in the first experiment in the table, calculated resistance = (46,970 × 72,450)/59,350 = 57,340; observed (III), 56,140. Difference in conductivity = 1/56,140 – 1/57,340 = 37.3 × 10^{-8} mho. Hence specific surface conductivity = 3.73 × 10^{-8} mho.

EXPERIMENTAL DATA ON INSOLUBLE FILMS IN CIRCULAR TROUGH (FIGURE 3)

The experiments of this section are presented in the form of three graphs› representing the effect of a film of oleic acid upon the time–resistance curves of conductivity water in the cell. After long investigation it was discovered that it is necessary to stir the surface thoroughly before the film is placed thereon; otherwise the mechanical disturbance accompanying the spreading of the film affects the resistance so seriously as to mask any surface conductivity which may be produced.

When the uncontaminated surface is stirred vigorously with a clean glass rod, the resistance *rises* immediately to a maximum and falls rapidly again after agitation ceases. The reason for this is either that atmospheric impurities are absorbed to form at the surface a thin conducting layer of solution which is replaced by pure water from the lower part of the cell during stirring, or that the highly cleaned surfaces of glass and platinum adsorb the impurities from the liquid in contact with them.

After the cell had been heated in a free flame, allowed to cool, and filled with conductivity water, tests with flowers of sulfur showed repeatedly that the surface of the liquid was clean and free from any premature contamination; the small particles could be blown about freely and without hindrance. Consequently the prior technique of brushing the surface with a paraffined rod was discontinued in the final experiments as probably superfluous.

Upon contamination with the oleic acid there is a rapid drop in resistance which is partly or wholly due to the surface conductance of the film. It has often been observed that a surface film tends to prevent contamination from the atmosphere, so that the total drop may be caused by surface conductance and not partially by solution of carbon dioxide or other contaminants from the enclosed atmosphere. When the acid film is disturbed by further stirring after contamination, a momentary rise in resistance takes place, which is attributed to a partial destruction of surface con-

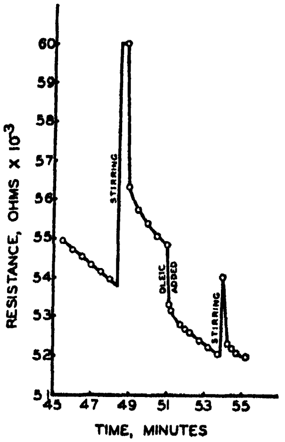

FIG. 4

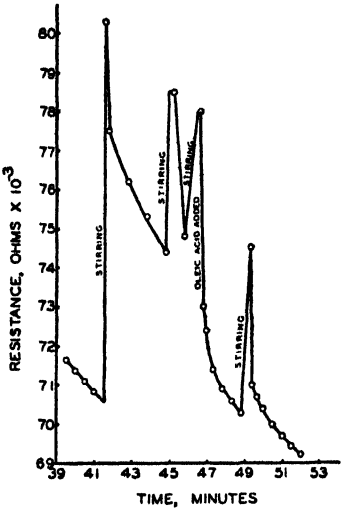

FIG. 5

FIG. 4. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)

Showing effects of stirring and instantaneous production of surface conductivity upon adding insoluble fatty acid.

FIG. 5. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)

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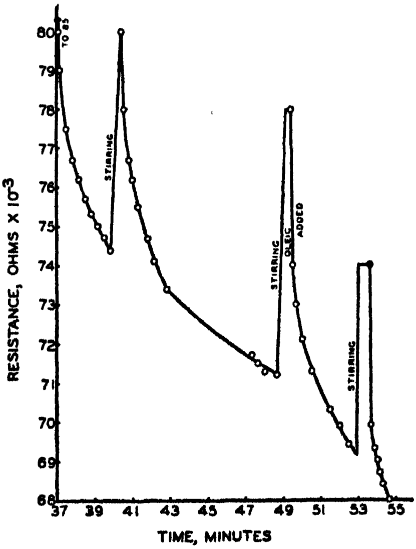

FIG. 6. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)

Showing effects of stirring and instantaneous production of surface conductivity upon adding insoluble fatty acid.

ductivity by disturbance of the double layer of ions at the interface, which is of course immediately restored.

Calculation of specific surface conductivity involves a selection of values of resistance which represent (I) resistance ot the cell without surface conductivity, and (II) resistance of the cell in the same condition as in (I) except for the addition of a surface film imparting a certain amount of surface conductivity. Such a selection is obviously somewhat arbitrary, although the order of magnitude of the surface conductivity thus calculated is unaffected by any reasonable choice. The experiment is too rapid for appreciable diffusion or alteration of bulk conductance, more especially as the oleic acid is practically insoluble.

It should again be emphasized that surface conductance so measured is merely the amount by which the surface conductance of the oleic film exceeds that of the uncontaminated air–water interface.

DISCUSSION

The outstanding result is the magnitude of the surface conductivity which uniformly exceeds 10^{-8} mho per square centimeter, sometimes by a very large factor, as in the last line of table 1, p. 7. This fully confirms the previous findings of McBain, Peaker, King, and collaborators. The results with glass tubing are very high on account of the microscopically visible irregularities of the surface.

The previously reported results for optically polished glass did not exceed 10×10^{-8} mho. Of course all glass which has ever been exposed to water or even water vapor is superficially decomposed and corroded chemically upon a molecular scale. This would tend to increase the effective above the apparent area, although, as has been pointed out (6), it is essentially only the projection of the molecular discontinuities in the direction of the current that is effective, and for the most part continuous passages of adequate cross section will be lacking. Hence this would not appear materially to affect the magnitude of the results. Another communication by DuBois and Roberts will present comprehensive electrokinetic studies with these same optical surfaces.

The ζ-potential found by DuBois and Roberts with 0.001 *N* potassium chloride by measurements of electrosmosis in the optically polished glass slit is -50 millivolts; DuBois (1) had used the value -78 millivolts derived from the data of Powis (10).

No uncertainty attaches to the similar results with the air–water interface, which is ideally plane. The surface conductivity therefore exceeds in order of magnitude that currently calculated[6] for the mobile ions of the diffuse part of the double layer.

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[6] For example, Bikermann (Z. Elektrochem. **38**, 763 (1932)) and Cole (Cold Spring Harbor Symposia on Quantitative Biology **1**, 27 (1933)). Bikermann in attempting

It is now well known (5) that the so-called double layer in its classical continuous form cannot exist, but that charges on any surface are far apart and often of different sign. Hence the continuous distribution postulated in the cloud of ions in the diffuse double layer, based upon Poisson continuity of electrical charge in the surface, does not in general occur in the neighborhood of the surface where strictly localized conditions prevail, although it may be built up at relatively remote distances. This is one more reason for disbelieving the real occurrence of the ζ-potentials classically or currently calculated.

TABLE 1

Deduction of surface conductivity in mhos × 10^8 of solutions of potassium chloride in contact with glass, assuming that the conductivity of 1 N potassium chloride is not appreciably influenced by surface conductivity

	CONCENTRATION				REMARKS
	N/1000	*N*/100	*N*/10	*N*/1	
Observed *R*	83,825	8,850	980.4	114.24	Measured on bridge
Conductivity of solvent (× 10^6)	0.5	0 4	0.7	0.7	Measured in another cell
Observed *R* corrected	84,110	8,850	980.4	114.24	Corrected for conductivity of solvent
Calculated *R* in tubes	69,878	7,263	795.5	91.72	Calculated from cross section, length, specific conductivity
R outside tubes	17,160	1,783	195.3	22.52	22.52 × ratios of specific conductivities
Observed *R* tubes	66,950	7,067	785.1	91.72	(Total observed *R*) − (*R* outside tubes)
Surface conductivity, K_s	62.6	382	1,660		$\frac{1}{R_{\text{obsd.}}} - \frac{1}{R_{\text{calcd.}}}$
Specific surface conductivity, k_s	9.96	60.8	264		$K_s \times 0.159 = k_s$

Surface conductivity is undoubtedly exhibited by all mobile ions whether in the diffuse part of the double layer or not, and also (Laing paradox) by all unbalanced ions attached to or within the surface. DuBois (1) has

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to defend the classical theory made the very serious error of abandonning in his calculation the well-known distinction between the Nernst potential ϵ and the electrokinetic potential ζ, taking the ζ-potential as 1 volt. His conclusions are therefore fallacious. A ζ-potential of 50 millivolts in his calculation would lead to the requirement that a film of water 0.4 A. U. thick had the viscosity and dielectric constant of water, although such a conclusion can carry but little weight if molecular dimensions retain any physical significance.

calculated from the data of McBain, Peaker, and King the individual surface conductances and mobilities which appear in the systems here considered.

TABLE 2

Surface conductivity of acid films on conductivity water (figure 2)

Cell constant (for surface conductivity): 1/10. Dimensions of electrodes (measured by Cambridge cathetometer): outer electrode (inside diameter), 1.932 cm.; inner electrode (outside diameter), 1.037 cm.

POSITION	RESISTANCE	POSITION	RESISTANCE	POSITION	RESISTANCE
Stearic acid		Stearic acid		Palmitic acid	
I	59,350	I	107,330	I	43,720*
II	72,450	II	150,360	II	48,610*
III	56,140	III	138,260	III	45,320*
IV	46,970	IV	104,450	IV	41,490*
$k_s = 3.73 \times 10^{-8}$		$k_s = 3\ 98 \times 10^{-8}$		$k_s = 3.87 \times 10^{-8}$	
Palmitic acid		Oleic acid		Oleic acid	
I	51,174*	I	49,785	I	44,546*
II	57,003*	II	64,150	II	50,110*
III	48,642*	III	55,640	III	43,757*
IV	44,574*	IV	45,270	IV	40,400*
$k_s = 4\ 18 \times 10^{-8}$		$k_s = 8\ 30 \times 10^{-8}$		$k_s = 8\ 48 \times 10^{-8}$	

* Cell + 100,000 ohm shunt.

TABLE 3

Surface conductivity of a film of oleic acid in a circular trough

Cell constant: 1/27. Resistance for continuous overflow, 170,000. Surface conductivity of oleic acid in closed cell (figure 2) was 8.4×10^{-8}

FIGURE NO.	*R* DURING STIRRING OF CONTAMINATED SURFACE (I)	*R* BEFORE DISTURBING ACID FILM (II)	$k_s \times 10^8$	*R* BEFORE CONTAMINATION (I)	*R* AFTER CONTAMINATION (II)	$k_s \times 10^8$
4	54,000	52,000	2.6	60,000	53,700	7.2
5	74,500	70,100	3 1	78,000	71,100	4.6
6	74,000	69,100	3 5	78,000	70,600	5 0

If this surface conductance is not sufficient there remain but two alternatives. The first is that which was suggested as reasonable by Horace Lamb (4), namely, that slip or sliding occurs between the two parts of the double layer, or between ions and the surface with which they are in contact, making all such ions mobile. Later authors have not endorsed this point of view, although some, like Smoluchowski, suspended judgment.

The other alternative, to adopt the terminology of Frenkel (2, 3) who has used it for explaining conductivity of dielectrics and supraconductivity of metals is "polarization current" carried by discontinuous jumps of otherwise sessile ions, the charge being thus transmitted from place to place. In the introduction we mentioned that a variety of polarization current might be exhibited with alternating current when it could not be produced by low voltages of direct current.

SUMMARY

Measurements extending over the past two years demonstrate the large surface conductivity per square centimeter exhibited by potassium chloride solutions in contact with glass surfaces, and likewise by films of fatty acid at the air–water interface. The specific surface conductivity of close packed films of stearic acid is 3.8×10^{-8} mho, that for palmitic acid 4.0×10^{-8} mho, and that for oleic acid 8.4×10^{-8} mho.

New designs of cells have been developed which permit a ready demonstration of these results.

These results are much too high to be attributable solely to the mobile ions in the outer portion of the diffuse double layer.

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CARBON DIOXIDE CLEAVAGE FROM DIBROMOMALONIC ACID

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The kinetics of the decomposition of carboxylic acids according to the scheme:

$$RCOOH \rightarrow RH + CO_2$$

has been studied several times. The type of acid which has been most thoroughly investigated is that of the β-ketocarboxylic acids. N. O. Engfeldt (6), E. Widmark (14), H. von Euler (7) and Ljunggren (10) have studied the decomposition of acetoacetic acid. Both the acid and the ion are unstable in aqueous solution. Amines catalyze the reaction. The decomposition of camphorcarboxylic acid and that of α-bromocamphorcarboxylic acid in water and in various organic solvents were studied by Bredig and his coworkers (2, 8, 11). These reactions were also catalyzed by amines.

β-Ketocarboxylic acids with a hydrogen atom in the α-position exist in two different forms, an enol and a keto form. The fact that both α- and γ-ketocarboxylic acids are stable has led to the hypothesis that the unstable form is the enol. K. J. Pedersen (13) has shown that α,α'-dimethylacetoacetic acid decomposes with even greater velocity than acetoacetic acid. The α,α'-dimethylacetoacetic acid cannot exist in the enol form, therefore in all probability the keto form is the unstable form.

Nitroacetic acid was studied by K. J. Pedersen (12) and J. F. Heuberger (9). The monovalent ion decomposes unimolecularly, while the undissociated acid is stable.

The acid used for the present investigation was dibromomalonic acid. The decomposition of this acid

$$Br_2C(COOH)_2 \rightarrow Br_2HCCOOH + CO_2$$

proceeds in aqueous solution even at room temperature with measurable velocity. The reaction velocity was studied at different hydrogen-ion concentrations and different salt concentrations. Dibromoacetic acid, which is a product of the reaction, was stable under these conditions. Most of the experiments were carried out at 25°C., a few at 35°C.

EXPERIMENTAL

Preparation of dibromomalonic acid

Dibromomalonic acid was prepared by the method of Conrad and Reinbach (5). The crude product was purified by dissolving it in ether, adding toluene, and concentrating the mixture *in vacuo* at room temperature until crystallization took place. Dibromomalonic acid is very soluble in ether and only slightly soluble in toluene, but addition of toluene to the ethereal solution in amount sufficient to precipitate the dibromomalonic acid does not yield the acid in the form of crystals, but gives rise to the formation of an oil or a mixture of oil and crystals. Also the addition of petroleum ether to the ethereal solution gave a mixture of crystals and oil. The product recrystallized from the ether–toluene mixture was pure, except for a small amount of dibromoacetic acid (about 1 per cent).

Experimental procedure

The velocity of the decomposition was determined by measuring the pressure of the evolved carbon dioxide during the reaction by means of an apparatus described by J. N. Brønsted (4). The concentration of dibromomalonic acid at the time t is proportional to $p_\infty - p$, where p_∞ is the pressure when the reaction is complete and p is the pressure at the time t. The reaction was studied in solutions containing hydrochloric acid and in buffer solutions. The initial concentration of dibromomalonic acid was in most experiments about 0.01 M; the concentration of the hydrochloric acid varied from 0.05 M to 1 M; the buffer concentration was usually about 0.1 M.

As dibromomalonic acid is a fairly strong acid and the concentration is not negligible compared with the buffer concentration used, it is necessary to know the dissociation constants in order to calculate the hydrogen-ion concentration of the mixtures.

Dissociation constants of dibromomalonic acid

The hydrogen-ion concentration in mixtures of the acid and its salts was measured electrometrically by means of a quinhydrone electrode. Three series of mixtures with different salt concentrations were made. To a weighed amount of dibromomalonic acid was added a known volume of a solution of sodium hydroxide and potassium chloride in such concentrations that the total salt concentration in the mixture after dissolution of the dibromomalonic acid was 0.1 N, 0.2 N, and 1 N, respectively. The solution was transferred into an electrode vessel fitted with a bright platinum electrode and quinhydrone. The potential of this electrode compared with a 0.1 N calomel electrode (connected through a saturated potassium chloride bridge) was read off as quickly as possible, and readings were continued every minute for ten minutes. Owing to the decomposition of dibromomalonic acid the potential falls off continually, but since the fall is practically linear in the first minutes, the initial value of the potential can be found by extrapolating to zero time. The potential was then determined, compared with the same calomel electrode, of an electrode with 0.01 *N* hydrochloric acid and potassium chloride to the same total salt concentration as that of the dibromomalonic acid solution.

The hydrogen-ion concentration was calculated by means of the formula

$$\mathrm{pH} = 2.000 + \frac{\pi_{\text{hydrochloric acid}} \div \pi_{\text{dibromomalonic acid}}}{0.0001984 \cdot 298}$$

where pH stands for the logarithm of the reciprocal of the hydrogen-ion concentration. $\pi_{\text{hydrochloric acid}}$ and $\pi_{\text{dibromomalonic acid}}$ are the potentials of the cells with hydrochloric acid and with dibromomalonic acid, respectively, at the same salt concentration. π is considered positive when the calomel electrode is the negative pole of the element.

TABLE 1

Concentration dissociation constants of dibromomalonic acid at different salt concentrations

Temperature, 25°C.

EQUIVALENT CONCENTRATION OF SALT	K_1	K_2
N		
0.1	1	9.0×10^{-3}
0.2	1	1.25×10^{-2}
1	1	1.70×10^{-2}

The two "concentration" dissociation constants can be calculated from the expressions

$$K_1 = C_{\mathrm{H}} \frac{C_{\mathrm{Br_2C(COOH)COO^-}}}{C_{\mathrm{Br_2C(COOH)_2}}} \quad \text{and} \quad K_2 = C_{\mathrm{H}} \frac{C_{\mathrm{Br_2C(COO^-)_2}}}{C_{\mathrm{Br_2C(COOH)COO^-}}}$$

or, if C_{acid} be the total concentration of dibromomalonic acid and C_{base} the initial concentration of sodium hydroxide:

$$K_1K_2(2C_{\text{acid}} - (C_{\text{base}} + C_{\mathrm{H}})) + K_1C_{\mathrm{H}}\,(C_{\text{acid}} - (C_{\text{base}} + C_{\mathrm{H}})) = C_{\mathrm{H}}^2(C_{\text{base}} + p_{\mathrm{H}})$$

The average values from several series of determinations are collected in table 1. These values (especially those of K_1) are only to be looked upon as approximate, owing to the magnitude of K_1 and K_2.

The dissociation constant of dibromoacetic acid at 0.1 *N* salt concentration was determined in a similar way and found to be $K = 6.9 \times 10^{-2}$.

Experiments in solutions of hydrochloric acid

The solutions were of three types: (1) x M hydrochloric acid, (1 − x) M potassium chloride; (2) x M hydrochloric acid, (0.2 − x) M potassium chloride; (3) x M hydrochloric acid, (0.1 − x) M potassium chloride. The reaction followed the first-order law

$$-kt = \log c + \text{const.} = \log (p_\infty - p) + \text{const.} \qquad (1)$$

The velocity constant was calculated by means of decadic logarithms, t being the time in minutes.

The results of the experiments are given in tables 2a, 3a, and 4a.

Experiments in buffer solutions

The solutions were of the following types: (1) x M hydrochloric acid, (0.1 − x) M glycine, (0.1 − x) M sodium chloride; (2) x M hydrochloric acid, (0.1 − x) M secondary sodium citrate; (3) x M hydrochloric acid, (0.2 − x) M glycine, (0.2 − x) M sodium chloride; (4) x M sodium hydroxide, 0.1 M citric acid + potassium chloride to a total salt concentration of 1 N; (5) x M acetic acid, (0.1 − x) M sodium acetate to a total salt concentration of 1 N; (6) x M hydrochloric acid, (0.2 − x) M glycine + potassium chloride to a total salt concentration of 1 N; (7) A few experiments were performed in solutions with double buffer concentration but with the same total salt concentration as in Nos. 4 and 5. M is the number of moles dissolved in 1 liter, neglecting reactions which may have taken place after mixing.

While the reaction in solutions of hydrochloric acid strictly follows the first-order law, k calculated from equation 1 in the experiments in buffer solutions falls off during the reaction. This is due to a decrease in the hydrogen-ion concentration accompanying the decomposition of dibromomalonic acid, and will be further discussed later on. The falling-off of k is not very marked, and the initial value of k can be determined with sufficient accuracy by extrapolating graphically to zero time. The values of k computed in this way are given in tables 2b, 2c, 2d, 3b, 4b, and 4c.

The hydrogen-ion concentration of the different buffer solutions can be calculated if the dissociation constants of the acids are known. At 0.1 N salt the following values found by Bjerrum (1) were used:

Glycine	$\mathrm{pK} = 2.359 - 0.041\sqrt[3]{c} + 0.18c$
Citric acid	$\mathrm{pK} = 3.080 - 0.46\sqrt[3]{c} + 0.18c$
Citric acid	$\mathrm{pK} = 4.799 - 1.04\sqrt[3]{c} + 0.18c$
Citric acid	$\mathrm{pK} = 6.443 - 1.71\sqrt[3]{c} + 0.18c$

TABLE 2

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 1 *N*

(a) HCl + KCl

HCl	DIBROMO-MALONIC ACID	c_H	pH	k	$\frac{k}{\alpha}$
M	*M*				
1.00			0	2.83×10^{-3}	5.7×10^{-3}
0.75	0.00924	0.755	0.122	3.25×10^{-3}	5.9×10^{-3}
0.50	0.01023	0.507	0.295	4.04×10^{-3}	6.2×10^{-3}
0.25	0.00977	0.258	0.588	4.53×10^{-3}	6.0×10^{-3}
0.20	0.00936	0.209	0.680	4.56×10^{-3}	5.9×10^{-3}
0.10	0.00853	0.109	0.963	4.48×10^{-3}	5.7×10^{-3}
0.08	0.00961	0.0907	1.042	4.22×10^{-3}	5.4×10^{-3}
0.05	0.00929	0.0612	1.213	4.10×10^{-3}	5.6×10^{-3}
0	0.0215	0.0290	1.54	3.31×10^{-3}	5.4×10^{-3}

(b) Glycine buffer + KCl

HCl	GLYCINE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.16	0.04	0.00962	0.90	4.58×10^{-3}	5.8×10^{-3}

(c) Citric acid buffer + KCl

CITRIC ACID	PRIMARY CITRATE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.18	0.02	0.00960	1.84	2.55×10^{-3}	5.5×10^{-3}
0.07	0.03	0.00912	2.18	1.49×10^{-3}	5.4×10^{-3}
0.05	0.05	0.00866	2.51	8.27×10^{-4}	5.5×10^{-3}
PRIMARY CITRATE	SECONDARY CITRATE				
M	*M*				
0.10	0	0.00861	3.20	1.92×10^{-4}	5.4×10^{-3}
0.08	0.02	0.00930	3.44	1.08×10^{-4}	5.2×10^{-3}
0.06	0.04	0.00970	3.70	6.90×10^{-5}	5.9×10^{-3}

(d) Acetic acid buffer + KCl

ACETIC ACID	ACETATE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.10	0.10	0.0211	4.14	2.01×10^{-5}	4.8×10^{-3}
0.04	0.06	0.0100	4.35	1.26×10^{-5}	4.8×10^{-3}
0.02	0.08	0.0100	4.71	5.1×10^{-6}	4.5×10^{-3}

TABLE 3

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 0.2 *N*

(a) HCl + KCl

HCl	DIBROMOMALONIC ACID	c_H	pH	k	$\frac{k}{\alpha}$
M	*M*				
0.20	0.00935	0.208	0.68	4.07×10^{-3}	5.1×10^{-3}
0.10	0.00934	0.1095	0.96	4.26×10^{-3}	5.2×10^{-3}
0.08	0.00936	0.0899	1.05	4.40×10^{-3}	5.4×10^{-3}
0.05	0.00907	0.0605	1.22	4.12×10^{-3}	5.1×10^{-3}

(b) Glycine buffer

HCl	GLYCINE	DIBROMOMALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.16	0.04	0.00939	0.89	4.37×10^{-3}	5.4×10^{-3}
0.14	0.06	0.00946	1.04	3.98×10^{-3}	4.9×10^{-3}
0.12	0.08	0.00930	1.24	3.85×10^{-3}	4.9×10^{-3}
0.10	0.10	0.00972	1.55	3.66×10^{-3}	5.4×10^{-3}
0.08	0.12	0.00920	1.97	2.54×10^{-3}	5.5×10^{-3}
0.06	0.14	0.00940	2.31	1.44×10^{-3}	5.1×10^{-3}
0.04	0.16	0.00928	2.62	7.72×10^{-4}	4.9×10^{-3}

TABLE 4

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 0.1 *N*

(a) HCl + KCl

HCl	DIBROMOMALONIC ACID	c_H	pH	k	$\frac{k}{\alpha}$
M	*M*				
0.10	0.00970	0.110	0.96	4.31×10^{-3}	5.0×10^{-3}
0.08	0.00932	0.0896	1.05	4.25×10^{-3}	5.0×10^{-3}
0.05	0.00959	0.0605	1.22	4.24×10^{-3}	5.1×10^{-3}

(b) Glycine buffer

HCl	GLYCINE	DIBROMOMALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.08	0.02	0.00952	1.20	4.18×10^{-3}	5.0×10^{-3}
0.07	0.03	0.00946	1.29	4.06×10^{-3}	5.0×10^{-3}
0.06	0.04	0.00921	1.46	3.76×10^{-3}	4.9×10^{-3}
0.05	0.05	0.00950	1.68	3.29×10^{-3}	4.9×10^{-3}
0.04	0.06	0.00979	1.96	2.78×10^{-3}	5.0×10^{-3}
0.03	0.07	0.00966	2.22	1.84×10^{-3}	4.6×10^{-3}
0.02	0.08	0.00938	2.50	1.20×10^{-3}	4.7×10^{-3}

TABLE 4—*Concluded*

(c) Citric acid buffer

HCl	SECONDARY CITRATE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.08	0.02	0.00937	1.29	4.25×10^{-3}	5.3×10^{-3}
0.07	0.03	0.00962	1.62	3.68×10^{-3}	5.3×10^{-3}
0.06	0.04	0.00947	2.34	1.58×10^{-3}	4.8×10^{-3}
0.05	0.05	0.00935	3.08	4.20×10^{-4}	4.9×10^{-3}
0.04	0.06	0.00955	3.64	9.97×10^{-5}	4.5×10^{-3}
0.03	0.07	0.00939	4.06	5.40×10^{-5}	5.6×10^{-3}
0.02	0.08	0.01013	4.30	2.3×10^{-5}	4.1×10^{-3}
0.01	0.09	0.00975	4.55	1.5×10^{-5}	4.9×10^{-3}

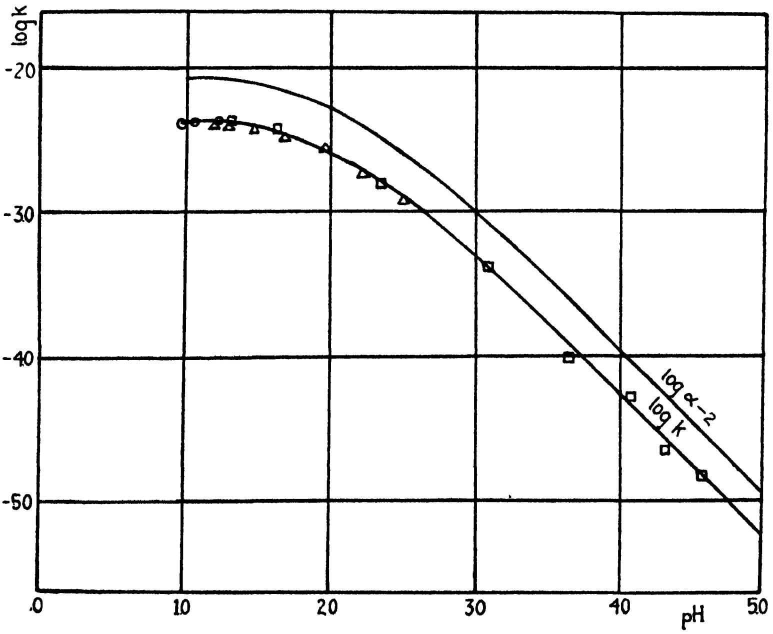

FIG. 1. EXPERIMENTS IN 1 *N* SALT SOLUTIONS

k, velocity constant of the decomposition of dibromomalonic acid.
α, fraction of dibromomalonic acid present as $Br_2C(COOH)COO^-$.
○ , experiments in solutions of hydrochloric acid and potassium chloride.
△ , experiments in solutions of glycine buffer and potassium chloride.
□ , experiments in solutions of citric acid buffer and potassium chloride.
▽ , experiments in solutions of acetic acid buffer and potassium chloride.

pK is the logarithm of the reciprocal of the concentration dissociation constant; c is the equivalent salt concentration. These formulas are valid up to 0.1 *N* salt concentration.

At 0.2 N and 1 N salt concentration no such values could be found in the literature, and it was necessary to determine the dissociation constants of glycine at 0.2 N salt concentration and of citric acid and acetic acid at 1 N salt concentration. This was carried out in a manner similar to that described for dibromomalonic acid. The results of the measurements were:

$$\begin{array}{lll} \text{Glycine} & K\ = 4.68 \times 10^{-3} & \ldots\ldots\ldots\ldots 0.2\,N \text{ salt at } 25^\circ\text{C.} \end{array}$$

$$\left.\begin{array}{ll} \text{Citric acid} & K_1 = 1.71 \times 10^{-3} \\ \text{Citric acid} & K_2 = 8.05 \times 10^{-5} \\ \text{Acetic acid} & K\ = 2.95 \times 10^{-5} \end{array}\right\} \ldots\ldots\ldots\ldots 1\,N \text{ salt at } 25^\circ\text{C.}$$

By means of these constants and those found for dibromomalonic acid the initial hydrogen-ion concentration in each experiment was calculated. In column 4 of tables 2, 3, and 4 the pH of the solutions is given. In figure 1 log k is plotted against pH. The curve shows a maximum at about pH 0.9; from pH ca. 2.5 it approaches a straight line.

Influence of temperature

A few experiments were carried out at 35°C. to determine the influence of temperature on the reaction velocity.

DISCUSSION

In solution dibromomalonic acid is present partly as the undissociated acid, partly as the ions $Br_2C(COOH)COO^-$ and $Br_2C(COO^-)_2$. On figure 1 log k and (log α − 2), where α is the fraction of dibromomalonic acid present as the univalent ion, are plotted against pH. The two curves seem to be very nearly parallel. This leads to the conclusion that the unstable compound is the univalent ion.

In the last column of tables 2, 3, and 4, k/α is given. This quantity is fairly constant over a wide range of pH, i.e.,

$$\frac{\mathrm{d} \log c}{\mathrm{d}t} = k = Q \cdot \alpha$$

where Q is a constant and c the total concentration of dibromomalonic acid, or

$$\frac{\mathrm{d}c}{\mathrm{d}t} = Q \cdot \alpha \cdot c$$

the rate of decomposition is proportional to the concentration of the univalent ion.[1]

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[1] According to the mass action law we have

$$K_1 = \frac{C_{\mathrm{H}} \cdot \alpha}{(1 - \alpha - \beta)} = \frac{k_w \cdot \alpha}{C_{\mathrm{OH}}(1 - \alpha - \beta)} \text{ and } K_2 = \frac{C_{\mathrm{H}} \cdot \beta}{\alpha}$$

α is proportional to $C_{\mathrm{H}} \cdot \beta$ and to C_{OH} $(1 - \alpha - \beta)$, and the constancy of k/α might just as well be explained by assuming hydrogen-ion catalysis on the divalent ion or hydroxyl-ion catalysis on the undissociated acid.

The $Br_2C(COO^-)_2$ ion seems to be stable. After two months at pH 10, no detectable amounts of carbonate were formed.

Whether or not the undissociated acid is stable cannot be demonstrated in aqueous solution, as the univalent ion even at pH 0 is present in an amount sufficient to conceal a possible decomposition of the undissociated acid. The decomposition of the acid might be shown by experiments in non-ionizing solvents. Such experiments are now in progress.

k/α is constant not only in the experiments in solutions of hydrochloric acid, but also in the buffer solutions. This indicates that there is no general acid or base catalysis.

According to Brønsted (3) the kinetic salt effect can be divided into two groups: (1) a primary salt effect, which consists in a direct influence on the reaction velocity of a reacting molecule, and (2) a secondary salt effect which is the influence on the reaction velocity caused by a change in the concentration of the reacting molecules. A thorough investigation of the salt effect requires experiments in very dilute solutions, but as the dibromomalonic acid is a fairly strong acid, this would involve great changes in the hydrogen-ion concentration and the salt concentration during the reaction, thus complicating the theoretical treatment of the experimental material.

TABLE 5

Experiments in 1 N salt solutions at 35°C.

HCl	DIBROMOMALONIC ACID	k	$k_{35°}/k_{25°}$	$k_{35°}/k_{25°}$ MEAN VALUE
M	*M*			
1.0	0.01	1.13×10^{-2}	4.08	4.01
0.5	0.01	1.58×10^{-2}	4.08	
0.2	0.01	1.86×10^{-2}	3.91	
0.1	0.01	1.83×10^{-2}	3.99	

In the present investigation experiments have been carried out at 0.1 *N*, 0.2 *N*, and 1 *N* salt concentrations. From the experimental data it will be seen that there is a marked secondary salt effect consisting in a change in the concentration of $Br_2C(COOH)COO^-$, while the primary salt effect is very small or zero. As already pointed out, there is a decrease in k during the reaction in the experiments in buffer solution. This may be due to a decrease in the hydrogen-ion concentration owing to the disappearance of the dibromomalonic acid.

Example 1. 0.05 *M* hydrochloric acid, 0.05 *M* glycine, 0.00930 *M* dibromomalonic acid:

At $t = 0$, pH = 1.68 $k_{\text{calcd.}} = 3.31 \times 10^{-3}$; $k_{\text{found}} = 3.29 \times 10^{-3}$

After 75 per cent decomposition, pH = 1.74 $k_{\text{calcd.}} = 3.17 \times 10^{-3}$; $k_{\text{found}} = 2.91 \times 10^{-3}$

Example 2. 0.06 M hydrochloric acid, 0.04 M secondary citrate, 0.00947 M malonic acid:

At $t = 0$, pH = 2.34 $k_{\text{calcd.}} = 1.62 \times 10^{-3}$; $k_{\text{found}} = 1.58 \times 10^{-3}$

After 75 per cent decomposition, pH = 2.51 $k_{\text{calcd.}} = 1.26 \times 10^{-3}$; $k_{\text{found}} = 1.40 \times 10^{-3}$

Since the determination of k is very inaccurate when the reaction is so far advanced, no better agreement with the calculated values could be expected.

At 35°C. the decomposition of dibromomalonic acid is too rapid to allow an electrometrical determination of the dissociation constants, but as the maximum velocity is found to be at about the same hydrogen-ion concentration as at 25°C., there seems to be no great change in these constants. Hence the results can be directly compared. The energy of activation calculated from the equation

$$E = R\,\frac{\mathrm{d}\log(k_2/k_1)}{\mathrm{d}(T^{-1})}$$

is found to be $E = 25{,}000$ calories per gram-molecule.

SUMMARY

The velocity of decomposition of dibromomalonic acid

$$Br_2C(COOH)_2 \rightarrow Br_2HCCOOH + CO_2$$

in aqueous solution at 25°C. has been studied at various hydrogen-ion concentrations and various salt concentrations.

At constant hydrogen-ion concentration the reaction follows the first-order law. The velocity is dependent upon the hydrogen-ion concentration.

The concentration dissociation constants were determined electrometrically at various salt concentrations.

The velocity was found to be proportional to the concentration of the $Br_2C(COOH)COO^-$ ion, i.e., the reaction can be described as a spontaneous decomposition of this ion. The velocity constant of the decomposition of the univalent ion in solutions containing 0.1 N salt was found to be 4.9×10^{-3} (min.$^{-1}$, decadic log.).

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THE INFLUENCE OF DEPOLARIZERS UPON THE PHOTOVOLTAIC EFFECT IN CELLS CONTAINING GRIGNARD REAGENTS[1]

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More than two hundred papers have appeared on the photovoltaic effect since Becquerel (1) reported his discovery of the effect in 1839. A review of the work that has been done, together with a summary of the theories that have been advanced, may be found in papers by Lifschitz and Hooghoudt (16) and by Dufford (7). A brief discussion is given by Hughes and DuBridge in their recent book (15).

An extensive study of the effect in Grignard compounds has been in progress at the Physical Laboratories of the University of Missouri for many years. Numerous compounds have been studied in connection with many different metals as electrodes. Measurable effects were observed in practically every case (2–6, 8–14, 17, 18).

All Grignard compound cells are easily polarized. In general the response to light is changed by electrical polarization. The polarization is probably produced by affecting the adsorbed layers on the electrodes. By observing the effect, if any, which depolarizers would produce, it was believed that additional light could be thrown upon the nature of these adsorbed layers. Hence this study was undertaken.

APPARATUS AND MATERIALS

The apparatus and experimental arrangements were essentially those used by Hammond (14) with only minor changes and improvements. The cells were made up in 1 in. by 8 in. test tubes which were covered with black friction tape except for 1½ in. at the bottom. One electrode was exposed below the friction-tape screen, and the other was above the lower edge of the screen, thus keeping it in darkness except for light diffused by the liquid or reflected from the exposed electrode.

Electrodes of copper, zinc, aluminum, iron, lead, and platinum were used in combination with two electrolytes and two depolarizers. The electrolytes were ethylmagnesium bromide and phenylmagnesium bromide solutions in ether. The depolarizers were ethyl bromide and ethyl iodide.

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[1] Abstracted from a thesis submitted to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics, August, 1932.

EXPERIMENTAL PROCEDURE

In making Grignard compounds, especial precaution was observed in keeping all glassware clean and dry. Every piece was washed thoroughly, allowed to stand in cleaning solution for at least twenty-four hours, again washed, rinsed with distilled water, and allowed to dry. The ether, which was kept over sodium in the storeroom, was distilled over sodium at least once, sometimes twice, before using. Molar solutions of the Grignard compounds in ether were made in the usual manner and diluted, in most cases, to 0.5 molar solution.

With only a few exceptions, all electrodes except platinum were brightly polished with steel wool just before inserting into the test tubes. In a few cases the oxides were left on the metals, and in a few other cases copper electrodes were coated with oxide by heating in an oxygen flame. Platinum electrodes were cleaned with nitric acid, washed thoroughly in distilled water, dried, and flamed.

The cells were allowed to stand in the dark, or in a relatively dark place, for at least thirty hours after being made up, before being put into the bath. There were a few exceptions to this practice when an attempt was made to determine the effect of standing. After being put into the bath, they were allowed to stand until the voltage became fairly constant, the time required varying from a few minutes to an hour.

A long series of observations was made on each cell before the depolarizer was added. After adding the depolarizer and thoroughly mixing, the cell was again allowed to stand in the dark for at least thirty hours. The same series of observations was made after depolarizing as before. Studies were made of (1) the dark voltage, (2) the voltage response to light, (3) current strength and current response to light when the cell was connected directly to the galvanometer with no external voltage in the circuit, (4) current strength and current response to light when an external voltage in series with the cell was applied from the potentiometer, causing a current to flow in such a direction as to make the illuminated electrode the anode, (5) current strength and current response to light when an external voltage made the illuminated electrode the cathode, (6) resistance and resistance response to light, taken after each of the observations 1 to 5 above, and (7) capacitance and capacitance response to light, taken simultaneously with the resistance readings. This was the general plan of study, and was carried out quite completely except for the resistance and capacitance. They were omitted from the study of many cells and were observed for some cells after only a part of the series of readings. In many other cases the resistance was measured without attempting to get the response to light.

In making these observations, it was the practice to continue taking readings at intervals of one minute or less until the quantity (voltage, current, or resistance) being measured changed relatively little or not at all during an interval. Usually this required from four to fifteen minutes.

A series of tests was made to determine the most effective quantity of depolarizer to add. The effect was studied for amounts varying from one drop to 10 cc. It was found that the effect on voltage and current responses to light increased with increasing amounts of depolarizer; but after 1 cc. was added the increase in the effect of the depolarizer was small. In the cases of resistance and capacitance the depolarizer seemed to produce no increased effect by adding more than 1 cc. Consequently, in most cases 1 cc. was used. The cells contained about 40 cc. of the Grignard solutions.

A cell was regarded as a resistance and capacitance in series, and the bridge equations used by Hammond (14) were employed with only slight simplifications.

As will be seen in the next section, voltage–time curves, current–time curves, resistance–time curves, and capacitance–time curves have been made showing responses to light in all the variations of the study. More than seven hundred curves were made, but only a few are included in this paper. The data when assembled consisted of five hundred seventy-six tables. Space does not, of course, permit the showing of more than a small fraction of this material, but an attempt has been made to select typical curves and data.

RESULTS

The writer believes that the curves and tables are, for the most part, self-explanatory. The notations concerning the curves and the headings of the tables were purposely made full and explicit. There are, nevertheless, a few cases where the notations are not entirely clear without explanation.

The curves are exhibited in pairs. The first curve shows the conditions before a depolarizer was added; the second, the conditions after the depolarizer was added. Arrows pointing upward indicate the time at which the light was turned on the cell, while arrows pointing downward indicate the time at which the light was turned off. The coördinates are the same for both curves; consequently they are omitted from the second curve of each pair. "No external voltage," as it occurs in the tables and with the curves, refers to the case where a cell has been short-circuited through the galvanometer for several minutes, thus allowing a current to flow, due alone to the E.M.F. of the cell. By "anode illuminated" is meant that a current has been sent through the cell from an external voltage for some time in

TABLE 1

Typical results

KIND OF CELL	DEPOLARIZER	DARK VOLTAGE, MILLIVOLTS		VOLTAGE RESPONSE, MILLIVOLTS		CURRENT, μμ A. PER. M.V., NO EXTERNAL VOLTAGE		CURRENT, μμ A. PER MV., ANODE ILLUMINATED		CURRENT, μμ A. PER MV., CATHODE ILLUMINATED		CURRENT RESPONSE, μμ A., NO EXTERNAL VOLTAGE		CURRENT RESPONSE, μμ A., ANODE ILLUMINATED		CURRENT RESPONSE, μμ A., CATHODE ILLUMINATED		RESISTANCE WITHOUT FORMING		RESISTANCE AFTER FORMING, NO EXTERNAL VOLTAGE		RESISTANCE AFTER FORMING, ANODE ILLUMINATED		RESISTANCE AFTER FORMING, CATHODE ILLUMINATED	
		No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
Pt/E_1/Pt	D_1	(2) 31.5	51.0	(3) −27.0	12.6	(12) 61.5	250	(6) 181.0	684.0	(5) 166	683.5	(9) −3,080	−1,760	(6) −6,160	−3,300	(5) −5,940	−1,760	(6) 33,370	44,890						
Pt/E_1/Pt	D_2	(5) 4.5	2.8	(5) −15.7	+3.2	(5) 388	1,040	(5) 458	1,500	(5) 453	1,040	(5) −3,300	+1,650	(5) −6,270	+1,430	(5) −1,100	+2,530	(1) 20,770	25,040	(1) 20,870	34,340	(1) 21,940	34,890	(1) 21,730	34,620
Pt/E_2/Pt	D_1	(6) 46.7	62.1	(6) −59.2	−45.4	(3) 327	313	(2) 398	450	(3) 444	463	(2) −21,850	−9,790	(2) −39,700	−15,300	(1) −12,420	−4,510	(1) 303,000	281,000	(1) 303,000	281,000				
Pt/E_2/Pt	D_2	(13) 18.2	33.0	(3) −48.3	−21.4	(2) 80.2	101.8	(1) 126.2	135.0	(1) 130.8	137.5	(1) −5,835	990	(1) −13,200	−1,320	(1) −220	−770								
Cu/E_1/Cu	D_1	(3) 165.9	63.5	(3) +100.1	+20.8	(3) 307	385	(3) 304	279.5	(3) 398	394	(3) +4,070	+1,650	(3) +35,700	+19,250	(3) +41,700	+24,400	(1) 4,590	21,540	(1) 4,612	21,740	(1) 4,634	22,310	(1) 4,660	22,130
Cu/E_1/Cu	D_2	(3) 6.6	20.5	(3) −50.0	−4.9	(3) 323.5	744.1	(2) 315	712	(2) 817	727			(1) −2,090	+18,700	(1) +4,400	−16,500	(1) 5,480	12,050	(1) 5,543	12,110				
Cu/E_2/Cu	D_1	(3) 1.6	12.5	(3) +30.0	+4.4	(2) 1,580	6,350	(2) 1,990	7,300	(2) 2,122	8,340	(2) 57,100	+27,700	(3) +34,100	+17,600	(2) +73,700	+12,200	(2) 78,190	51,100	(2) 78,180	51,950	(2) 78,790	51,750	(2) 78,300	52,400
Cu/E_2/Cu	D_2	(3) 1.6	6.2	(3) +1.4	+5.2	(3) 4,230	6,760	(1) 664	234	(1) 285	231	(3) +14,520	+27,300	(2) +26,700	+37,600	(2) +16,500	+21,900	(2) 16,940	15,500	(2) 17,220	15,670	(2) 17,460	15,750	(2) 17,920	15,920
Al/E_1/Al	D_1	(4) 27.2	4.9	(4) +4.7	+0.7	(4) 18,186	372,054	(4) 24,017	047,725	(4) 2,091	062,790	(4) +4,950	+467,000	(4) +3,300	+1,622,000	(4) +4,290	+1,765,000	(1) 5,077	1,670	(1) 5,154	1,570	(1) 5,867	1,050	(1) 5,339	1,030
Al/E_1/Al	D_2	(2) 11.4	1.0	(2) +6.3	+0.7	(2) 1,360	11,550	(1) 676	1,169	(4) 679	1,074	(2) +7,150	+36,800	(1) +4,400	+3,960	(1) +15,400	+2,860	(1) 8,413	3,880	(1) 8,553	3,764				
Al/E_2/Al	D_1	(2) 4.0	2.9	(2) +53.7	+11.6	(2) 3,722	46,800			(2) 79.2	382	(2) +3,410	+43,500	(2) −1,100	−26,400	(2) +41,300	+6,600	(2) 43,000	6,020	(2) 43,300	6,060	(2) 43,000	6,088	43,150	6,054
Al/E_2/Al	D_2	(2) 11.6	16.2	(2) +68.8	+92.3	(2) 6.3	254,000	(2) 70.2	274,000	(2) 73.0	271,000	(2) +2,090	279,000	(2) +6,050	+43,300	(2) +41,150	+118,900	(2) 48,200	22,960	(2) 48,800	23,470	(2) 50,880	23,340	49,600	23,810
Fe/E_1/Fe	D_1	(3) 3607	1.2	(2) −8.0	−3.5	(3) 58.8	1466	(3) 138	199	(3) 126.6	16.4	(2) −2,970	−13,640	(3) −7,810	+4,510	(3) −1,210	+550	(1) 4,990	27,180	(1) 5,185	27,490	(1) 22,800	28,440	(1) 5,314	28,160
Fe/E_1/Fe	D_2	(2) 150.6	102.0	(2) +65.9	+2.0	(2) 271	396	(2) 281	423	(1) 619	448														
Fe/E_2/Fe	D_1	(3) 5.1	5.6	(2) +8.7	+0.4	(2) 255	692	(2) 328	547	(2) 258	622	(2) +4,400	+3,400	(2) −4,400	−1,100	(2) +8,800	+4,400	(2) 40,600	35,050	41,540	35,160	43,690	35,750	43,090	35,450
Fe/E_2/Fe	D_2	(2) 8.0	7.0	(2) +7.9	+12.3	(2) 202	275	(2) 142.5	143.5	(2) 172	195.2	(3) +1,540	+1,760	(3) −4,950	−880	(3) +11,000	+15,400	(2) 67,500	24,500	(2) 67,400	24,400	(2) 61,800	22,600	(2) 66,200	24,280
Zn/E_1/Zn	D_1	(4) 20.9	5.0	(4) +6.2	+1.1	(4) 17,050	23,301	(4) 28,952	31,900	(3) 28,900	34,950	(4) +1,650	+550	(4) +4,950	+4,560	(3) +4,730	+771	(1) 40,090	36,940	(1) 40,400	37,100	(1) 39,340	37,500	(1) 39,070	37,400
Zn/E_1/Zn	D_2	(3) 10.0	19.0	(2) +8.1	+3.5	(2) 378	1,530	(2) 1,060	1,620	(2) 1,073	1,595	(2) +6,160	+5,830	(1) −6,490	+5,610	(1) +12,870	+7,260	(1) 48,800	736,600	(1) 113,200	708,700				
Zn/E_2/Zn	D_1	(3) 7.5	13.7	(3) +23.6	+28.2	(3) 302	183.5	(1) 2,920	28.9	(1) 2,880	310	(2) +6,940	+15,500	(3) +12,100	+3,300	(3) +2,200	31,900	(3) 85,990	60,590	(3) 87,300	61,400	(3) 389,500	57,700	(3) 88,400	57,700
Zn/E_2/Zn	D_2	(2) 1.5	0.6	(2) +20	+1	(2) 167	12,100	(1) 11,700	178,000	(1) 11,700	39,300	(2) +1,210	+222,000	(2) −9,900	+285,000	(2) +15,720	+282,000	(2) 19,300	3,270	(2) 19,470	3,176	(2) 19,910	3,198	(2) 20,000	3,193
Pb/E_1/Pb	D_1	(2) 16.4	4.0	(2) +7.3	+6.4	(2) 572	1,030	(2) 436	1,135	(2) 412	1,135	(2) +7,360	+4,285	(2) +2,200	+3,300	(1) +32,000	+4,285	(1) 5,710	16,800	(1) 5,931	16,300	(1) 5,996	16,890	(1) 5,975	16,590
Pb/E_1/Pb	D_2	(2) 9.5	14.5	(2) +0.7	+2.4	(2) 16,500	162,450	(2) 27,500	142,500	(2) 27,500	142,500	(2) +17,600	4,428,000	(2) −96,800	−279,300	(2) −17,600	+3,351,600	(1) 26,310	2,726	(1) 26,670	2,720	(1) 28,130	2,960	(1) 27,730	2,920
Pb/E_2/Pb	D_1	(8) 11.0	10.1	(8) +7.1	+4.7	(2) 879	1,168	(2) 1,222	1,780	(2) 932	1,525	(2) +8,360	+4,180	(1) −9,900	−5,500	(1) +33,200	+15,400	(1) 132,860	84,370	(1) 135,800	86,130	(1) 135,800	87,810	(1) 112,070	87,810
Pb/E_2/Pb	D_2	(2) 1.6	1.7	(2) +0.7	+3.2	(2) 20,200	23,000	(2) 22,000	11,450	(2) 21,100	18,950	(2) +2,310	+16,200	(2) 3,570	+59,400	(2) +3,520	+35,400	(2) 26,150	13,120	(2) 26,760	13,110	(2) 27,460	13,350	(2) 27,030	13,210

TABLE 2

Typical results—Continued

KIND OF CELL	DEPOLARIZER	RESISTANCE RESPONSE, WITHOUT FORMING		RESISTANCE RESPONSE AFTER FORMING, NO EXTERNAL VOLTAGE		RESISTANCE RESPONSE AFTER FORMING, ANODE ILLUMINATED		RESISTANCE RESPONSE AFTER FORMING, CATHODE ILLUMINATED		CAPACITANCE, M.F., WITHOUT FORMING		CAPACITANCE, M.F., AFTER FORMING, NO EXTERNAL VOLTAGE		CAPACITANCE, M.F., AFTER FORMING, ANODE ILLUMINATED		CAPACITANCE, M.F., AFTER FORMING, CATHODE ILLUMINATED		CAPACITANCE RESPONSE WITHOUT FORMING		CAPACITANCE RESPONSE AFTER FORMING, NO EXTERNAL VOLTAGE		CAPACITANCE RESPONSE AFTER FORMING, ANODE ILLUMINATED		CAPACITANCE RESPONSE AFTER FORMING, CATHODE ILLUMINATED	
		No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
Pt/E_1/Pt	D_1	(1) + 210	+ 510	(1) + 270	+ 30					(1) 0 23296	0 10364	(1) 0 21857	0 8530					(1) 0 00244	- 0 00122						
Pt/E_1/Pt	D_2									(1) 4 65	2.23	(1) 4 49	0 437	(1) 1 29	0 153	(1) 2 14	0 425								
Pt/E_2/Pt	D_1																								
Pt/E_2/Pt	D_2																								
Cu/E_1/Cu	D_1			(1) - 15	+ 50					(1) 7 7005	1 9900	(1) 7 3742	1 9150	(1) 7.09	1 697	(1) 6 73	(1) 1 869			(1) 0 1163	- 0.014				
Cu/E_1/Cu	D_2	(1) + 8	+ 70	(1) + 6	+ 57					(1) 7 225	3 55	(1) 7 186	3 4898					(1) + 0 607	- 0 0919	(1) - 0.060	- 0 0844				
Cu/E_2/Cu	D_1							(2) + 430	+ 300	(2) 0 1475	0 198	(2) 0 159	0 191	(2) 0 156	0 187	(2) 0 1585	0 1868							(1) 0 0019	0 0019
Cu/E_2/Cu	D_2	(1) + 90	+ 55	(1) + 53	+ 50	(1) + 90	+ 60	(1) + 70	+ 60	(2) 0 559	0 132	(2) 0 511	0 130	(2) 0 457	0 114	(2) 1 005	2 090	(1) - 0 053	- 0 06	(1) - 0 027	- 0 056	(1) - 0 04	- 0 04	(1) - 0.015	- 0 02
Al/E_1/Al	D_1									(1) 2 57		(1) 2 40		(1) 2.62		(1) 2 62									
Al/E_1/Al	D_2	(1) + 32	+ 9	(1) + 19	+ 10					(1) 2.6959	2 75	(1) 2 49	2 745					(1) - 0 0425	- 0 03	(1) - 0 02	+ 0 03				
Al/E_2/Al	D_1	(1) + 85	+ 50	(1) + 115	+ 57	(2) + 90	+ 70	(1) + 120	+ 50	(1) 0 462	7 08	(1) 0 491	6 74	(1) 0.3983	6 243	(2) 1 3758	1 4933	(1) - 0 00499	- 0 2331	(1) - 0 0383	- 0 0223				
Al/E_2/Al	D_2	(1) + 200		(1) + 150				(2) + 380	+ 200	(2) 0 243	0 1885	(2) 0 223	0.178	(2) 0.216	0 182	(2) 0 2258	0 1758	(1) - 0 035		(1) - 0 027				(1) - 0 00380	- 0 00312
Fe/E_1/Fe	D_1	(1) 0 00	+ 230	(1) 0 00		(1) + 250	+ 120	(1) 0 00		(1) 1 3392	0 54709	(1) 1 518	0 56685	(1) 0.80128	0 53481	(1) 1 5313	0 53354	(1) 0 00	+ 0 02914			(1) - 0 0233	- 0 00595		
Fe/E_1/Fe	D_2																								
Fe/E_2/Fe	D_1	(1) + 130	+ 137	(1) + 460	+ 210	(1) + 200	+ 145	(1) + 220	+ 166	(2) 0 534	0 781	(2) 0 50377	0 74175	(2) 0.446	0.691	(2) 0 462	0 703	(1) - 0 0704	- 0 1216	(1) - 0 01348	- 0 01180				
Fe/E_2/Fe	D_2	(1) + 360		(1) + 340	+ 190	(1) + 440		(1) + 500	+ 280	(2) 0 249	0 422	(2) 0 2492	0 426	(2) 0 2655	0.474	(2) 0.2592	0.1535			(1) - 0 02612	- 0 0189			(1) - 0 00434	- 0 0037
Zn/E_1/Zn	D_1			(1) + 290	+ 130					(1) 0 45506	1 1377	(1) 0.68022	0.86006	(1) 1.8109	0.8345	(1) 0.74857	0.8409			(1) - 0 01066	- 0 00842				
Zn/E_1/Zn	D_2																								
Zn/E_2/Zn	D_1			(1) + 200	+ 200					(2) 0 219	0 0301	(2) 0.0219	0 0312	(3) 0 02195	0.0288	(3) 0 0216	0.0298								
Zn/E_2/Zn	D_2	(2) + 250	+ 20	(2) + 350	+ 9	(2) + 140	+ 6	(2) + 150	- 6	(2) 1.491		(2) 1.451		(2) 1 3468		(2) 1 698		(2) - 0.031		(2) - 0 043		(2) - 0.0121		- 0 046	
Pb/E_1/Pb	D_1			(1)	+ 130					(1) 7.8536	2 4415	(1) 5.8049	1.9479	(1) 5.6035	1.736	(1) 5 748	1.823			(1)	- 0.0586				
Pb/E_1/Pb	D_2	(1) + 120	+ 8.0	(1) 110	10					(1) 1.001		(1) 0 94505	1.989	(1) 0.79433	1.6111	(1) 0 86002	0.9236	(1) - 0.115				(1) - 0 01676	- 0 0498		
Pb/E_2/Pb	D_1																								
Pb/E_2/Pb	D_2	(1) + 390	+ 350			(1) + 230	+ 150			(2) 1 495	2.76	(2) 1.125	2.86	(2) 0.91532	2.6538	(2) 1 097	2.675	(1) - 0.00541	- 0 02837			(1) - 0 02142	- 0 1288		

such a direction that the electrode exposed for illumination was the anode. It does not mean that the anode was always illuminated at the time the measurement was made.

When the light causes the voltage of the irradiated electrode to become more positive, or less negative, with respect to the dark electrode, the change is called a "positive response." If the light produces the reverse effect, the change is called a "negative response." A positive resistance response or a positive capacitance response is a change in which the resistance or capacitance of the cell is increased by the action of light. A current response is defined as positive when the change in current would indicate a positive voltage response, assuming the resistance of the cell to remain constant.

The current in micromicroamperes per millivolt was determined by the equation

$$I = \frac{f \times d}{V \pm E}$$

with E positive when the external voltage was in the direction of the E.M.F. of the cell, and negative when in the opposite direction. V was, of course, zero for cases of no external voltage. In each case f is the figure of merit of the galvanometer, expressed in micromicroamperes per millimeter, d the deflection in millimeters, E the terminal voltage of the cell, and V the external voltage applied. E and V are in millivolts.

The following symbols will be used in the discussion of results:

D = depolarizer.
D_1 = ethyl bromide as depolarizer.
D_2 = ethyl iodide as depolarizer.
E_1 = ethylmagnesium bromide as electrolyte.
E_2 = phenylmagnesium bromide as electrolyte.
E_1-D_1 = a cell having E_1 as electrolyte and D_1 as depolarizer.
$\mathrm{Pt} \mid E_1\ (+D_1) \mid \mathrm{Pt}$ = a cell having platinum electrodes with E_1 as electrolyte and D_1 as depolarizer.

Tables 1 and 2 are introduced for the purpose of summarizing the results of the whole study. The results given are as nearly typical as could be selected. The blank spaces indicate that no results were obtained. While it was the policy to use the results from the same cell in a given row, this was not always done. For example, in a group $\mathrm{Pt} \mid E_1\ (+D_1) \mid \mathrm{Pt}$ cells, the voltage response might be of one cell and the resistance of another. The numbers in parentheses indicate the number of cells from which the most typical result was selected.

The results are set out in such detail by the curves and tables that an extensive discussion seems quite unnecessary. However, a brief summary may not be undue repetition.

Platinum electrodes

An examination of the curves, figures 1 to 3, and tables 1 and 2 shows that (1) responses to light were negative before the addition of a depolarizer,

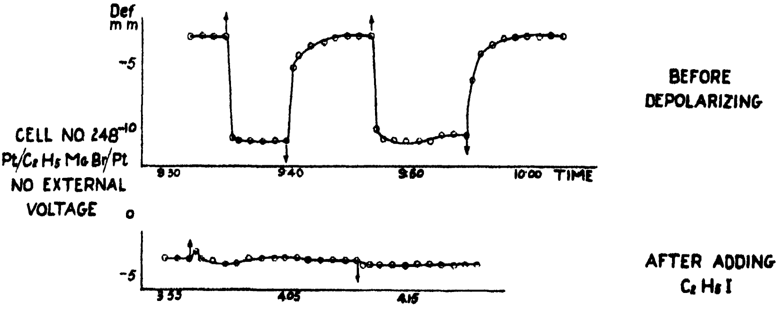

FIG. 1

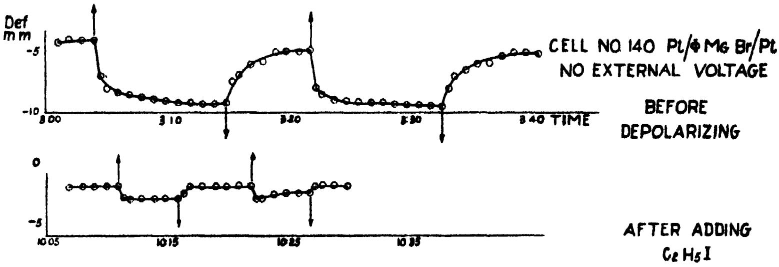

FIG. 2

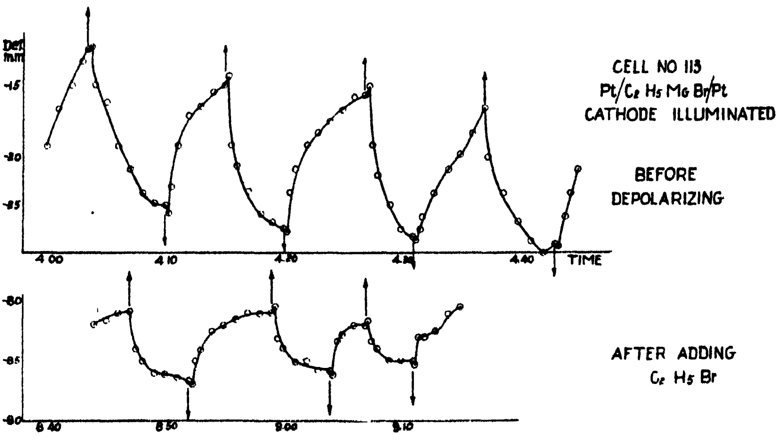

FIG. 3

(2) the addition of either depolarizer reduced the responses, (3) with E_2 the addition of either depolarizer produced no change in the direction of the

responses, and (4) the addition of D_1 to E_1 caused a reversal of the direction of the responses.

The dark E.M.F. was not consistently affected by either depolarizer, but the dark current was usually greatly increased. Increases as great as twelvefold were observed when D_1 was added to E_1.

The resistance of cells containing E_1 was increased by adding either depolarizer, while that of cells containing E_2 was decreased by D_1. Insufficient data are available to show the effect of D_2 on the resistance of E_2 cells.

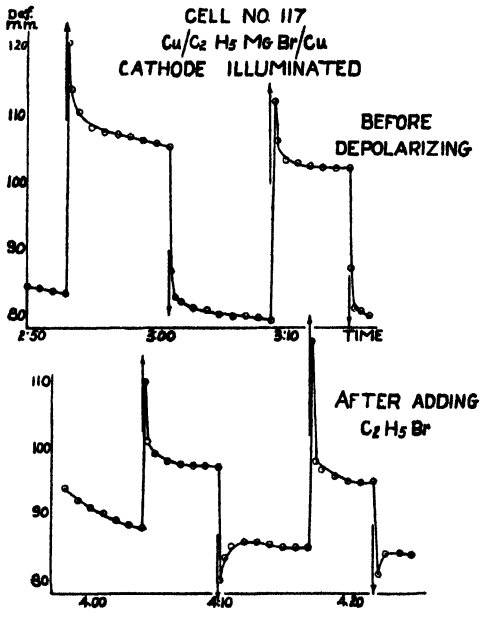

FIG. 4

Capacitance ranged from 0.10 microfarad to 4.65 microfarads, varying widely with the same type of cell. The addition of D_1 or D_2 to E_1 produced a decrease in capacitance.

The results with platinum electrodes, shown in table 2, on resistance and capacitance responses are no more than slightly indicative since only one cell is reported.

Copper electrodes

The curves for cells having copper electrodes are quite characteristic. Figure 4 shows that the responses were almost instantaneous. Within a very few seconds after the light was turned on or off, the galvanometer (in the case of current responses) reached a maximum deflection and started back. This peculiar effect may be due, at least in part, to an exceedingly thin coating of cuprous oxide.

Voltage and current responses to light are in general positive both before and after the addition of depolarizers. The effect of either depolarizer on the magnitude of the responses is much less in evidence with copper than with platinum electrodes, but where consistent effects were observed the responses were found to be reduced.

Both depolarizers seem to have increased the resistance of cells containing E_1. Cells containing E_2 showed much smaller resistances after adding D_1, but apparently were little affected by the addition of D_2. Resistance responses were uniformly small and positive with one exception. The response was greater with E_1 cells after adding either depolarizer, but with E_2 cells the response was less after adding D_2.

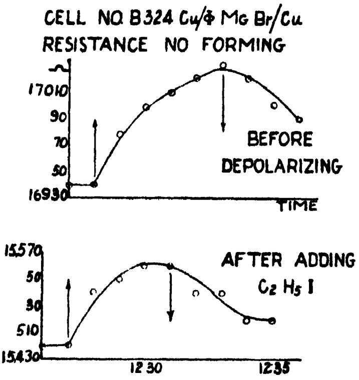

FIG. 5

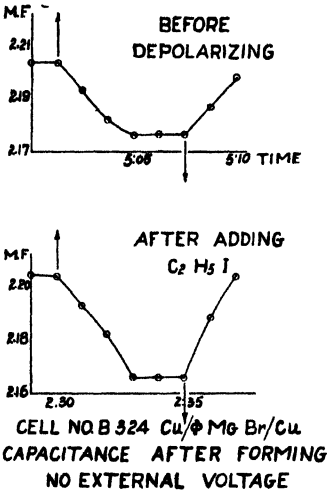

FIG. 6

E_1 cells had a much higher capacitance than E_2 cells. The capacitance of E_1 cells was strikingly smaller after adding either depolarizer, but D_1 seemed more effective than D_2. Cells containing E_2 exhibited slight increases in capacitance on adding D_1, but rather large decreases after the addition of D_2. Capacitance responses were almost uniformly negative. The writer believes that the exceptions are due to some extraneous cause. While the responses are small, there seems to be little doubt that they are present. Figure 6 shows two capacitance curves exhibiting the responses quite clearly. A decrease in capacitance response was observed in cells containing E_1 after adding either D_1 or D_2, but D_1 apparently increased slightly the response in the one cell containing E_2.

Iron electrodes

Reference here will be made only to resistance and capacitance measurements. The resistance of E_2 cells was higher than the resistance of E_1 cells. The resistance of E_1 cells was decreased by D_1, while the resistance of E_2 cells was decreased by both D_1 and D_2. Resistance responses were as a rule relatively large, though barely over 1 per cent. Figure 7 shows an example of the responses obtained. No case of negative response was found.

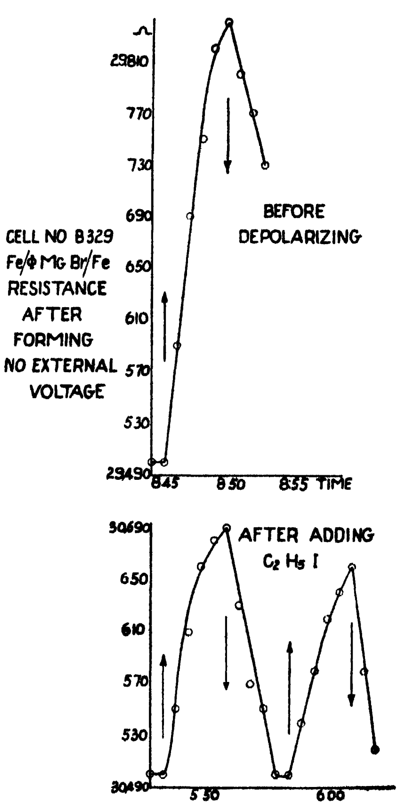

FIG. 7

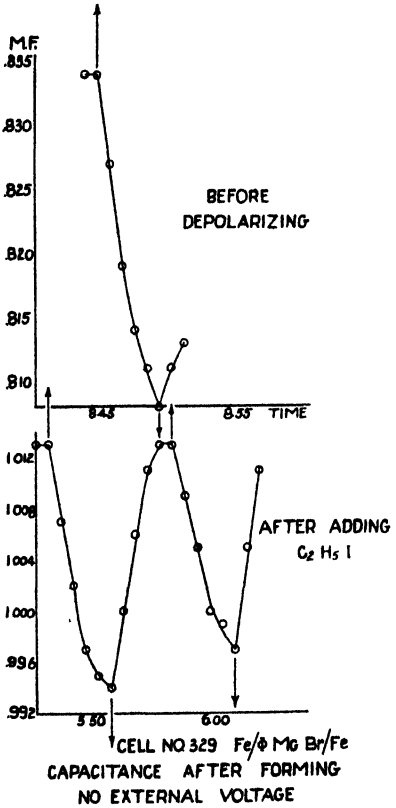

FIG. 8

The capacitance of iron cells was unusually low, seldom reaching 1 microfarad. While the E_1 cells showed a higher capacitance than the E_2 cells, the difference was less conspicuous for iron electrodes than for any other. D_1 apparently produced a decrease in the capacitance of E_1 cells, while both depolarizers seemed to have increased the capacitance of E_2 cells. Capacitance responses were uniformly negative. A typical response is exhibited in figure 8.

Among the iron cells were a few that produced alternating current. Figure 9 is a current-time curve of such a cell.

A GENERAL VIEW OF THE RESULTS

Further details of results cannot be given in this paper, but as stated above, the curves and tables are purposely made self-explanatory.

Nothing was said in the previous discussion regarding the dark voltage. There was nothing to say. The value of the dark voltage occurs, within limits, as if it were a matter of chance. It ranges usually from 0 to 40 millivolts, but sometimes runs to more than 100. There is no doubt that there are sufficiently good reasons for this behavior, but they have not yet been discovered.

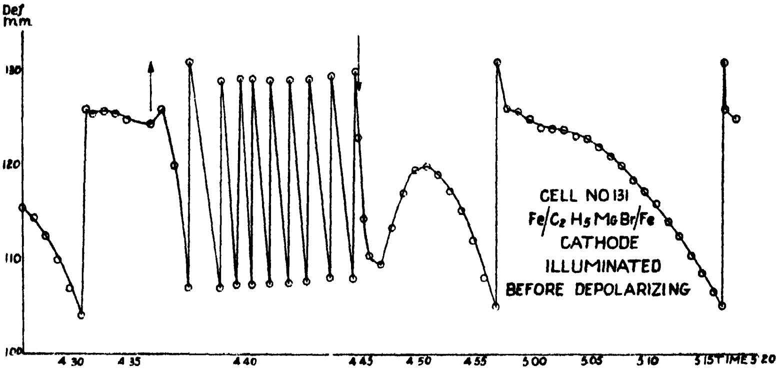

FIG. 9

The effect of the "forming" process, i.e., of polarizing the electrodes either anodically or cathodically, has been apparently ignored, but again the omission was intentional. An examination of the data fails to reveal any uniformity in effects due to the process of "forming."

The so-called Minchin reversal is very clearly shown in figure 3. Unusual care is necessary to catch and record these quick reversals. They take place as a rule, within 3 to 6 seconds.

THEORETICAL CONSIDERATIONS

A consideration of the theories that have been advanced to explain the photovoltaic effect shows that each is based upon either the chemical action of light, the photoelectric effect, or the effect of excited molecules on or near the electrode. The general arguments for and against these theories may be found in the references cited above. The arguments favoring the excited molecule theory seem to be most convincing just now, and the findings herein reported are certainly more in line with this theory than with any other.

The size of a molecule of a short-chain, aliphatic compound, like ethylmagnesium bromide, is believed to be smaller than that of a molecule of an aromatic compound, such as phenylmagnesium bromide. If the layer on an electrode is monomolecular in thickness, as Hammond's calculations indicate, the layer of ethylmagnesium bromide should be thinner than the layer of phenylmagnesium bromide. Consequently the capacitance of the condenser composed of the film separating the electrolyte and the surface of the plate should be greater for the cells filled with ethylmagnesium bromide. This agrees with the experimental findings. On the other hand, the resistance offered by the film might be expected to be proportional to some function of the thickness, leading to the conclusion that the phenylmagnesium bromide cells should have the higher resistance to direct current. This was found to be true.[2]

In studies by Langmuir and others, it has been found that in certain monomolecular layers the molecules are particularly oriented with respect to the surface. It is then not unreasonable to suppose a similar condition in the cases under consideration.

Now, if light produces in and near these layers a number of excited molecules which have different dipole moments from normal molecules, and which have the property of displacing normal molecules from the layers, an altered difference of potential would result. The change in difference of potential would increase until a kind of saturated layer of excited molecules was built up on the electrode. The life period of these excited molecules may be short, so that when the light is turned off and thus no more are being produced to replace the "dead" ones on the surface, the electrode "recovers in the dark" and the difference of potential becomes normal.

Change in A. C. resistance must indicate a change in the electrolyte, which at present is thought to be due to change in condition of solvation of ions, resulting in their altered mobility.

The assumption that a double layer, containing in the outer film only a comparatively few molecules, is formed, or altered, when the light is turned on, would explain the negative capacitance response. This assumption becomes quite plausible when one considers the polarized condition of the excited molecules.

By assuming that the negative "ends" of the polarized molecules attach themselves to some metals, while with other metals the positive "ends" are so attached, one can explain the fact of positive and negative voltage and current responses.

---

[2] Hammond arrived at these same conclusions.

Any substance, such as the depolarizers used in this study, when added to a cell, would quite likely disturb the layer on the electrodes. Just what effect the added substance would have would probably depend upon the electrolyte, the electrodes, and the substance added.

To explain completely, on the basis of this theory, the observed effects of the depolarizers, would require more information on the chemical reactions involved, and especially on the structure of the molecules, than is at present available.

The writer desires to acknowledge his indebtedness and express his appreciation to Professors R. T. Dufford and H. E. Hammond of the Department of Physics of the University of Missouri, to President Eugene Fair of the Northeast Missouri State Teachers College, and to Mrs. Harty for assistance in this study. Professor Dufford suggested and directed the investigation, Professor Hammond helped in perfecting the experimental arrangements, President Fair furnished much-needed financial assistance, and Mrs. Harty took many of the readings. The work was begun and carried about half through at the University of Missouri, and completed at the Teachers College.

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ON THE MECHANISM OF POTENTIAL FORMATION IN A SOLUTION OF FOREIGN IONS

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As was shown by us previously (1) in the most simple cases of the sharply expressed selective adsorption of one of the sort of the foreign solution ions by the metal, the connection between the potential and the concentration (more accurately, the activity) of the ions may be written:

$$E = \pm \frac{2RT}{nF} \ln \frac{K_1}{K_2} \pm (2m - 1) \frac{RT}{nF} \ln cf \tag{1}$$

The experiments described in the preceding paper have confirmed this equation for the potential of gold in the solutions of copper sulfate, copper nitrate, and silver nitrate.

In the present paper are offered the results of further experiments on the study of the potentials of metallic silver in solutions of copper salts. To this end, exactly as with the earlier method, were measured the E.M.F. of the cells

$$\mathrm{Ag} \mid \mathrm{CuSO_4} \mid \mathrm{NH_4NO_3}\ \text{saturated} \mid 1N\ \mathrm{KCl, Hg_2Cl_2} \mid \mathrm{Hg}$$

and

$$\mathrm{Ag} \mid \mathrm{Cu(NO_3)_2} \mid \mathrm{NH_4NO_3}\ \text{saturated} \mid 1N\ \mathrm{KCl, Hg_2Cl_2} \mid \mathrm{Hg}$$

from the values of which were calculated the potentials of silver in corresponding concentrations of solutions. Simultaneously the potentials of copper in the same electrolytes were measured. The graphic and analytic comparisons of both potentials show that between them there is rectilinear dependence, that is:

$$\left.\begin{array}{ll} & E_{\mathrm{Ag/CuSO_4}} = a + bE_{\mathrm{Cu/CuSO_4}} \\ \text{and} & E_{\mathrm{Ag/Cu(NO_3)_2}} = a + bE_{\mathrm{Cu/Cu(NO_3)_2}} \end{array}\right\} \tag{2}$$

The values for the potentials of silver and copper, found by experiment, and the values of the constants a and b are given in tables 1 and 2.

As the potential of copper in a solution of copper salts may be expressed by Nernst's equation, that is,

$$E_{\mathrm{Cu/CuSO_4}} = E^0_{\mathrm{Cu/CuSO_4}} + \frac{RT}{2F} \ln C_{\mathrm{Cu^{++}}} f_{\mathrm{Cu^{++}}}$$

TABLE 1

$CuSO_4$	$E_{\mathrm{Ag/CuSO_4}}$ (at 20°C.)	$E_{\mathrm{Cu/CuSO_4}}$	$\Delta_1 = E_{\mathrm{Ag/CuSO_4}} - 0.420$	$\Delta_2 = E_{\mathrm{Cu/CuSO_4}} - 0.2725$	$b = \frac{\Delta_1}{\Delta_2}$
N					
2.0	+0.5430	+0.3215	+0.1230	0.0490	2.53
1.5	0.5351	0.3185	0.1151	0.0460	2.50
1.0	0.5313	0.3150	0.1113	0.0425	2.61
0.75	0.5284	0.3120	0.1084	0.0395	2.74
0.5	0.5145	0.3095	0.0945	0.0370	2.55
0.25	0.4933	0.3030	0.0733	0.0305	2.40
0.125	0.4831	0.2990	0.0631	0.0265	2.38
0.0125	0.4440	0.2820	0.0240	0.0095	2.52
Mean value of *b*					2.54
Mean value of *a*					−0.296

TABLE 2

$Cu(NO_3)_2$	$E_{\mathrm{Ag/Cu(NO_3)_2}}$	$E_{\mathrm{Cu/Cu(NO_3)_2}}$	$\Delta_1 = E_{\mathrm{Ag/Cu(NO_3)_2}} - 0.32$	$\Delta_2 = E_{\mathrm{Cu/Cu(NO_3)_2}} - 0\ 182$	$b = \frac{\Delta_1}{\Delta_2}$
N					
7.0	+0.5609	+0.4298	+0.2409	+0.2478	0.97
5.0	0.5312	0.4082	0.2112	0.2262	0 93
3.0	0.5127	0.3820	0.1927	0.2000	0.96
2.0	0.5060	0.3658	0.1860	0.1838	1.01
1.5	0.4934	0.3569	0.1734	0 1749	0.99
1.0	0.4868	0.3468	0.1668	0.1648	1.01
0.75	0.4800	0.3402	0.1600	0.1582	1.01
0.50	0.4770	0.3331	0.1570	0.1511	1.04
0.0125	0.4365	0.3079	0.1165	0.1259	0.92
0.00125	0.4240	0.2979	0.1040	0.1159	0.90
Mean value of *b*					0.97
Mean value of *a*					+0.1431

and

$$E_{\mathrm{Cu/Cu(NO_3)_2}} = E^0_{\mathrm{Cu/Cu(NO_3)_2}} + \frac{RT}{2F} \ln C_{\mathrm{Cu^{++}}} f_{\mathrm{Cu^{++}}}$$

then by substituting the value for the potential of copper in equation 2, and by putting in the numerical values of the constants *a* and *b*, we have:

$$E_{\mathrm{Ag/CuSO_4}} = (2.54\,E^0_{\mathrm{Cu/CuSO_4}} - 0.296) + 2.54\,\frac{RT}{2F}\ln C_{\mathrm{Cu^{++}}}f_{\mathrm{Cu^{++}}},\ \text{i.e., } m = 1.77$$

and

$$E_{\mathrm{Ag/Cu(NO_3)_2}} = (0.974\,E^0_{\mathrm{Cu/Cu(NO_3)_2}} + 0.143) + 0.974\,\frac{RT}{2F}\ln C_{\mathrm{Cu^{++}}}f_{\mathrm{Cu^{++}}},\ \text{i.e., } m = 0.987$$

TABLE 3

KBr	$E_{\mathrm{Cu/KBr}}$ (AT 18°C.) (A. Schmid)	$f_{\mathrm{Br^-/KBr}}$ (AT 25°C.) (Landolt)	$E_{\mathrm{Br_2/KBr}} =$ 1.087–0.058 ln cf	$\Delta_2 = E_{\mathrm{Br_2/KBr}} - 1.138$	$b = \frac{E_{\mathrm{Cu/KBr}}}{\Delta_2}$
N					
0.01	+0.144	0.90	+1.2056	+0.0676	2.13
0.10	−0.034	0.776	+1.1514	+0.0134	(−2.53?)
1.00	−0 037	0.630	1.098	−0.0400	2.17
2.00	−0.121	0.614	1.0818	−0.0562	2.15
3.00	−0.144	0.616	1 0715	−0.0665	2.16
4.00	−0 171	0.626	1.0639	−0.0741	2.30
Mean value of b					2.18
Mean value of a					−2.484

TABLE 4

KBr	$E_{\mathrm{Cu/KBr}}$ (AT 18°C.) (A. Schmid)	$f_{\mathrm{Br^-/KBr}}$ (AT 25°C) (Haas-Jellinek)	$E_2 = E_{\mathrm{Br_2/KBr}} = 1.087 - 0.058$ ln cf	$\Delta_2 = E_2 - 1.14$	$b = \frac{E_{\mathrm{Cu/KBr}}}{\Delta_2}$
N					
0 01	+0 144	0.895	+1.2057	+0 0657	2.19
0.10	−0.034	0.720	1.1533	+0.0133	(−2 55?)
1.00	−0.087	0.590	1.1002	−0.0398	2.18
2.00	−0.121	0.584	1.0832	−0.0569	2.12
3.00	−0 144	0.577	1 0732	−0.0668	2.15
4 00	−0.171	0.570	1.0663	−0 0737	2.32
Mean value of b					2.19
Mean value of a					−2.500

Thus the potential of silver in solutions of copper salts, like the potential of gold, is caused by the selective adsorption of the cations of the electrolyte (Cu^{++}) on the surface of the metal, and obeys equation 1.

In order to check the theory advanced by us here on the measurements of A. Schmid and Winkelmann (4), we have proceeded as follows: As the potentials of copper in solutions of halogen salts of potassium and sodium become more electronegative by an increase of solution concentration, i.e., as if they had an anion character, then it may be assumed that the potentials are explained by the selective adsorption of the anion. Therefore the values of the potentials of chlorine and bromine were calculated (according to Nernst's equation) for the corresponding concentrations of the solutions of sodium chloride, potassium chloride, and potassium bromide. The values of the activity coefficients for these electrolytes were taken from two sources,—the "mean" activity coefficients from Landolt's tables (3), and the "true" from the paper of Haas and Jellinek (2).

TABLE 5

NaCl	$E_1 = E_{Cu/NaCl}$ (at 18°C.) (A. Schmid)	$f_{Cl^-/KCl}$ (at 25°C.) (Landolt)	$E_2 = E_{Cl_2/KCl} = 1.36 - 0.058 \ln cf$	$\Delta_1 = E_1 + 0.13$	$\Delta_2 = E_2 - 1.30$	$b = \frac{\Delta_1}{\Delta_2}$
N						
0.01	+0.123	0.904	+1.4785	+0.253	0.1785	1.4?
0.10	+0.076	0.789	1.4240	0.206	0.1240	1.6?
1.00	+0.002	0.659	1.3705	0.132	0.0705	1.9
2.00	−0.026	0.667	1.3528	0.104	0.0528	1.9
3.00	−0.052	0.709	1.3410	0.078	0.0410	1.9
4.00	−0.087	0.767	1.3318	0.043	0.0318	1.3?
5.00	−0.096	0.860	1.3233	0.034	0.1233	1.4?
Mean value of *b*.						1.63
Mean value of *a*.						−2.245

TABLE 6

KCl	$E_1 = E_{Cu/KCl}$ (at 18°C.) (A. Schmid)	$f_{Cl^-/KCl}$ (at 25°C.) (Landolt)	$E_2 = E_{Cl_2/KCl} = 1.36 - 0.058 \ln cf$	$\Delta_1 = E_1 + 0.13$	$\Delta_2 = E_2 - 1.138$	$b = \frac{\Delta_1}{\Delta_2}$
N						
0.01	+0.123	0.899	+1.4787	+0.253	+0.1620	1.6 (?)
0.10	+0.086	0.764	1.4248	0.216	0.1081	2.0
1.00	−0.008	0.597	1.3730	0.122	0.0563	2.1
2.00	−0.043	0.569	1.3573	0.087	0.0406	2.1
3.00	−0.070	0.570	1.3465	0.060	0.0298	2.0
4 00	−0.087	0.581	1.3398	0.043	0.0231	1.9
Mean value of *b*.						2.0
Mean value of *a*.						−2.78

The comparison of the potentials of copper with those of chlorine and bromine show that in these cases the rectilinear dependence of type

$$E_{Cu/MeX} = a + bE_{X_2/MeX}$$

holds, but there are certain deviations, especially for sodium chloride. The data from A. Schmid's papers, the potentials of chlorine and bromine, calculated by "mean" and "true" activity coefficients, and the values of constants *a* and *b* are given in tables 3, 4, 5 and 6.

As there are no marked differences between *a* and *b* for potassium bromide in both cases, in the future the values for *f* will be taken only from Landolt's tables.

Thus the potentials of copper in solutions of halide salts of alkali metals, measured by A. Schmid and his collaborators, are explained by the selective adsorption of electrolyte anions and are subordinated to equation 1, taken in this case for anion adsorption, i.e., with the minus sign placed before the logarithm of activity. In agreement with the values of *a* and *b* given in the tables, equation 1 may be written:

For Cu/KBr:

$$E_{\mathrm{Cu/KBr}} = (2.18\,E^0_{\mathrm{Br/KBr}} - 2.484) - 2.18\,\frac{RT}{F}\ln C_{\mathrm{Br^-}} f_{\mathrm{Br}}\;,\ \text{i.e.,}\ m = 1.59$$

For Cu/NaCl:

$$E_{\mathrm{Cu/NaCl}} = (1.63\,E^0_{\mathrm{Cl_2/NaCl}} - 2.245) - 1.63\,\frac{RT}{F}\ln C_{\mathrm{Cl^-}} f_{\mathrm{Cl^-}}\,,\ \text{i.e.,}\ m = 1.31$$

For Cu/KCl:

$$E_{\mathrm{Cu/KCl}} = (2\,E^0_{\mathrm{Cl_2/KCl}} - 2.78) - 2\,\frac{RT}{F}\ln C_{\mathrm{Cl^-}} f_{\mathrm{Cl^-}}\,,\qquad \text{i.e.,}\ m = 1.5$$

Taking into consideration the imperfection in the calculations of the same manner (the potentials of chlorine and of bromine are not found experimentally, but only by calculation), it is possible to consider that there is satisfactory agreement between equation 1 and the given experimental data of A. Schmid.

SUMMARY

1. In addition to the preceding measurements of the potential of gold in solutions of copper and silver salts, the potentials of silver in solutions of copper sulfate and copper nitrate were measured.

2. The dependence (deduced earlier on the basis of the adsorption theory for such potential) between the potential and the activity of the selectively adsorbed ions, proved on the potential of gold, was confirmed by the potential of silver and by the experimental data of A. Schmid and his collaborators (the potential of copper in the halogen solutions of alkali metals).

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OXIDATION AND REDUCTION WITH HYDROGEN PEROXIDE

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In suitably acid solutions and with suitable concentrations hydrogen peroxide reduces the following: cobaltic sulfate to cobaltous sulfate; lead peroxide to lead sulfate; permanganic acid, manganese dioxide, and manganic sulfate to manganous sulfate; chlorine and hypochlorous acid to hydrochloric acid; bromic acid to hydrobromic acid and bromine; chromic acid to chromic sulfate; chloric acid at 80°C. to hydrochloric acid and chlorine; hypobromous acid to hydrobromic acid; thallic sulfate to thallous sulfate; bromine to hydrobromic acid; periodic acid to iodic acid; iodic acid to iodine; 95 per cent nitric acid to oxides of nitrogen; bismuth pentoxide to bismuth trioxide; pentavalent vanadium to tetravalent vanadium.

In suitably acid solutions and with suitable concentrations hydrogen peroxide oxidizes the following: hydrochloric acid to chlorine; hydrobromic acid to bromic acid; hydriodic acid to iodine and to iodic acid; ferrous chloride to ferric chloride; nitrous acid to nitric acid; mercurous nitrate to mercuric nitrate; silver to silver sulfate; tetravalent vanadium to pentavalent vanadium; cuprous chloride to cupric chloride; ferrocyanic acid to ferricyanic acid; stannous chloride to stannic chloride; hydroxylamine and nitrous acid to nitric acid; nickel and lead to the corresponding sulfates.

In suitably alkaline solutions and with suitable concentrations hydrogen peroxide reduces the following: potassium permanganate and manganate to manganese dioxide; potassium ferrate to ferric oxide; silver peroxide and silver oxide to silver; potassium hypobromite to bromide; potassium ferricyanide to ferrocyanide; nickelic oxide to nickelous oxide; bismuth pentoxide to bismuth tetroxide (or Bi_4O_7); potassium periodate to iodate; and potassium hypoiodite to iodide. It is said, though wrongly, to reduce mercuric oxide to mercurous oxide.

In suitably alkaline solutions and with suitable concentrations hydrogen peroxide oxidizes the following: potassium cyanide to cyanate; sodium sulfite to sulfate; lead and lead monoxide to lead peroxide; bismuth trioxide to bismuth tetroxide (or Bi_4O_7); cobaltous oxide to cobaltic oxide or peroxide; manganous and manganic oxides to manganese peroxide; vanadium tetroxide to vanadium pentoxide; chromic oxide to potassium chromate; thallous oxide to thallic oxide; nitric oxide and potassium nitrite to potassium nitrate; cuprous oxide to cupric oxide; hydroxylamine to nitrogen; ferrous and stannous oxides to ferric and stannic oxides, respectively; zinc to sodium zincate.

It is not claimed that this is a complete list of the oxidations and reductions with hydrogen peroxide, but these instances will suffice to show the apparent complexity of the problem. So far as the theoretical side of the subject is concerned, the literature is in a state of chaos because the "misleading experiment" has tripped up everyone. The problem has not been and cannot be solved by a phenomenological study alone. The Baconian method is not adapted to this sort of work.

Fredenhagen (11) and Bornemann (4) both accept Haber's view of two potentials for hydrogen peroxide in acid solution, a reducing potential at about $E_h = +0.8$ volt and an oxidizing potential at about $E_h = +1.4$ volts. Bornemann says that "a substance with a potential in a dilute acid solution smaller than $E_h = +0.8$ volt, such as hydriodic acid with about $E_h = 0.5$ volt, can only be oxidized by molar hydrogen peroxide. If the potential of the reacting substance is higher than $E_h = +1.4$ volts, such as $E_h = +1.5$ volts for potassium permanganate, there can only be reduction by hydrogen peroxide. Substances with potentials between $E_h = +0.8$ volt and $E_h = +1.4$ volts may be either reduced or oxidized by hydrogen peroxide. When the nature of the substance permits of either reduction or oxidation, which will happen or whether both will happen simultaneously to an appreciable extent depends only on relative reaction velocities; catalytic agents play an important part within this range."

Our experiments show that there are no true electromotive forces for dilute hydrogen peroxide in acid solution at about $E_h = +0.8$ volt and about $E_h = +1.4$ volts, and that there is no range within which it is a question of reaction velocity whether reduction or oxidation occurs. There is also no true electromotive force for hydrogen peroxide at about $E_h = +1.66$ volts as postulated later by Haber (16). In the same way the normal electrode potential $E_h = +1.8$ volts, as given by Kremann and Müller (18) for the alleged reaction $H_2O_2+2H = 2H_2O$, is entirely mythical. Bray (5) gives $E_h = +1.78$ volts.

The real relation is quite simple. If the true electromotive force, referred to the normal hydrogen electrode, for any oxidizing or reducing agent in any solution is larger than the true electromotive force of hydrogen peroxide in the same solution, that substance will be reduced by hydrogen peroxide. If the true electromotive force, referred to the normal hydrogen electrode, of any oxidizing or reducing agent in any solution is smaller than the true electromotive force of hydrogen peroxide in the same solution, that substance will be oxidized by hydrogen peroxide. As will be shown later, the reason why this relation has not been clear from the beginning is that people talked about measured electromotive forces and not about true electromotive forces.

In tables 1 and 2 are given data for some of the oxidizing and reducing agents which are on record as reacting with hydrogen peroxide. The figures under E_c(Murphy) were obtained at Cornell and are measurements made against the normal calomel electrode. Platinum wires were used and were heated electrically (34) to bring them approximately to equilibrium. The plus sign denotes that the calomel electrode is anode. The E_c data have been converted into E_h values by adding 0.300 volt, with no other correction for liquid-junction potentials except for the reversible reaction between iodic acid and iodine, where the measurements were made against hydrogen in molar sulfuric acid. The E_c data are not necessarily right, but they are comparable. The E_h data, not based on our E_c measurements, are taken from the literature and are not comparable among themselves or with the Cornell data. So far as can be judged, they are right relatively to hydrogen peroxide; but no guarantee can be given that they are right absolutely or right relatively to each other.

To many people this will seem a deplorable state of affairs. They will feel that we should have corrected all these data and that we should have given our data at least to millivolts and probably to tenths of millivolts. T. W. Richards once said that to measure a thing ten times as accurately meant one hundred times the work. There is a great deal of time wasted on unnecessary accuracy in measurements. If we wish to know whether hydrogen peroxide will oxidize ferrous chloride at all, we must determine the electromotive force of a practically pure ferrous chloride solution. If we wish to know whether hydrogen peroxide will oxidize ferrous chloride completely, we must determine the electromotive force of a practically pure ferric chloride solution. The spread in this case is more than 0.2 volt, so an accuracy of millivolts means nothing. The corresponding spread for tetravalent to pentavalent vanadium is apparently nearly half a volt. From the admittedly inaccurate data in table 1 we shall see that the best measurements of the electromotive force for appreciable concentrations of hydrogen peroxide in acid solution may be roughly 0.3–0.4 volt too low.

There will undoubtedly come a time when it will be desirable to measure these electromotive forces to millivolts or less. For the moment the important thing is the determination of general relations. That has been overlooked entirely in the forty years of exact measurements and elaborate thermodynamics. It is usually stated that it is a waste of time to measure the electromotive forces of practically pure ferrous sulfate and ferric sulfate, because the electromotive force measurement means nothing unless we define the concentrations of the reaction products. This may be true theoretically; but we deny it very often when we do a potentiometric analysis. It would be a distinct help if people made and tabulated the electromotive forces which are involved in potentiometric analyses, instead of ignoring them or treating them as belonging in an entirely independent chapter.

It is quite clear from table 1 that, in approximately molar solutions of hydrochloric or sulfuric acid, all oxidizing and reducing agents having an electromotive force for the reaction and concentrations in question larger than about $E_h = +1.16 \pm 0.3$ volts are reduced by hydrogen peroxide. All having an E_h value smaller than about 1.16 ± 0.03 volt are oxidized by hydrogen peroxide. This does not mean that hydrogen peroxide will oxidize ferric chloride higher because the reaction measured is $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$. If we should or could measure the reaction $Fe^{III} \rightleftharpoons Fe^{VI}$ that electromotive force would be found to be larger than $E_h = +1.16$ volts.

TABLE 1

Behavior of hydrogen peroxide in acid solutions

E_c (Murphy) data are mostly in M HCl or M H_2SO_4. Parentheses denote that the enclosed constituent is present in relatively small amounts

REACTION	REDUCTION		REACTION	OXIDATION	
	Approximate E_h	E_c (Murphy)		Approximate E_h	E_c (Murphy)
$O_3 \rightarrow O_2$*	+1.80		$I_2 \rightarrow (HIO_3)$	+1.15†	+0.850
$Co_2(SO_4)_3 \rightarrow CoSO_4$	+1.79		$HBr \rightarrow (Br_2)$	+1.09	+0.790
$PbO_2 \rightarrow PbSO_4$	+1.63	+1.325	$HNO_2 \rightarrow HNO_3$	+0 94	
$HMnO_4 \rightarrow MnSO_4$	+1.54	+1.237	$(FeCl_2) \rightarrow FeCl_3$	+0 90	+0.60
$HBrO_3 \rightarrow Br_2$	+1.44	+1.14	$Hg_2(NO_3)_2 \rightarrow Hg(NO_3)_2$	+0 87	
$MnO_2 \rightarrow MnSO_4$	+1.43		$Ag \rightarrow Ag_2SO_4$	+0 67	+0.37
$Cl_2 \rightarrow HCl$	+1.37		$HI \rightarrow I_2$	+0.62	
$HBrO \rightarrow HBr$	+1.35		$Cu_2Cl_2 \rightarrow CuCl_2$	+0 55	
$HClO_3 \rightarrow HCl$	+1.34	+1.058	$H_2SO_3 \rightarrow H_2SO_4$	+0 49	+0.19
$H_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3$	+1.29	+0.99	Ferrocyanic acid→ferri-		
$Br_2 \rightarrow (HBr)$	+1.26	+0.96	cyanic acid	+0.44	
$Tl_2(SO_4)_3 \rightarrow TlSO_4$	+1.21		$NH_2OH \rightarrow HNO_2$	+0.35	+0.05
$(HIO_4) \rightarrow HIO_3$	+1.20	+0.899	$SnCl_2 \rightarrow SnCl_4$	+0.2	
$HIO_3 \rightarrow (I_2)$	+1.17†	+0.867	$Pb \rightarrow PbSO_4$	−0.29	−0.589

* One-way reactions; not strictly reversible.

† Measured directly and not calculated.

The data in table 1 show that the true electromotive force of hydrogen peroxide in a solution approximately molar with respect to hydrogen ion is about $E_h = +1.16 \pm 0.3$ volts, and that there is no intermediate range within which relative reaction velocities determine whether oxidation or reduction will occur. The directly measured value of about $E_h = +0.8$ volt and the deduced value of $E_h = +1.66$ volts go by the board.

It is quite clear from table 2 that, in approximately molar solutions of potassium hydroxide, all oxidizing and reducing agents having an electromotive force for the reaction and concentrations in question larger than about $E_h = +0.30 \pm 0.03$ volt are reduced by hydrogen peroxide. All having an electromotive force smaller than about $E_h = +0.30 \pm 0.03$ volt are oxidized by hydrogen peroxide, with the exception of potassium iodide to potassium iodate, which will be discussed later. When an oxidation or reduction can only go one way under the conditions of the experiment, the predictions apply only to the reaction measured. We can obtain approximate values for the oxidation of sulfurous acid to sulfuric acid and for the oxidation of alkaline sodium sulfite to alkaline sodium sulfate, but the reverse reaction does not take place at all in alkaline solutions; in acid solutions it takes place only at very high concentrations of sulfuric acid.

TABLE 2

Behavior of hydrogen peroxide in alkaline solutions

E_c (Murphy) data are mostly in *M* KOH

REACTION	REDUCTION		REACTION	OXIDATION	
	Approximate E_h	E_c (Murphy)		Approximate E_h	E_c (Murphy)
$KMnO_4 \rightarrow K_2MnO_4$	+0.73	+0.43	$PbO \rightarrow PbO_2$	+0.27	−0.030
$K_2FeO_4 \rightarrow Fe_2O_3$	+0.71	+0.41	$KI \leftarrow KIO_3$*	+0.16	−0.145
$NaClO \rightarrow NaCl$*	+0.70	+0.40	$Hg \rightarrow HgO$	+0.15	−0.15
$K_2MnO_4 \rightarrow MnO_2$	+0.59	+0.294	$KCN \rightarrow KCNO$	+0.13	−0.175
$Ag_2O_2? \rightarrow Ag_2O$	+0.58		$Na_2SO_3 \rightarrow Na_2SO_4$*	+0.11	−0.19
$Bi_2O_5 \rightarrow Bi_2O_4$	+0.58	+0.279	$Bi_2O_3 \rightarrow Bi_2O_4$	+0.11	−0.19
Ferricyanide→ferrocyanide	+0.51	+0.214	$MnO \rightarrow MnO_2$	+0.11	−0.19
			$CoO \rightarrow Co_2O_3$	+0.10	−0.20
$Ni_2O_3 \rightarrow NiO$	+0.51	+0.21	$Cr_2O_3 \rightarrow K_2CrO_4$*	+0.08	−0.22
$KIO_4 \rightarrow KIO$	+0.44		$Tl_2O \rightarrow Tl_2O_3$	+0.05	
$Ag_2O \rightarrow Ag$	+0.34	+0.038	$KNO_2 \rightarrow KNO_3$	+0.01	
			$Cu_2O \rightarrow CuO$	−0.08	
			$NH_2OH \rightarrow N_2$*	−0.29	−0.59
			$Pb \rightarrow PbO$	−0.56	
			$FeO \rightarrow Fe_2O_3$	−0.83	
			$SnO \rightarrow SnO_2$	−0.87	
			$Zn \rightarrow Na_2ZnO_2$	−1.118	

* One-way reactions; not strictly reversible.

The data in table 2 show that the true electromotive force for hydrogen peroxide in a solution approximately molar with respect to hydroxyl ion is about $E_h = +0.3 \pm 0.03$ volt, and that there is no intermediate range within which relative reaction velocities determine whether oxidation or reduction will occur. This compares with an apparent value as measured directly and not corrected for diffusion potentials of about $E_h = +0.04$ volt.

It must be remembered that the value of $E_h = +0.3 \pm 0.03$ volt contains the acid–alkali liquid-potential difference, which is not present in the value of $E_h = +1.16 \pm 0.03$ volts. Consequently these two values cannot be compared directly.

There is independent evidence for $E_h = +1.16$ volts being somewhere near the true electromotive force for hydrogen peroxide in approximately molar hydrochloric acid or sulfuric acid. No one has ever obtained the theoretical value of 1.23 volts for the oxyhydrogen gas cell, but values up to 1.15 volts have been measured by independent observers. Over fifty years ago Traube (48) showed that hydrogen peroxide is formed when oxygen is reduced at the cathode. Both G. N. Lewis (21) and Haber (15) drew the natural conclusion that the primary reaction in the oxyhydrogen gas cell is the formation of hydrogen peroxide. This view has not yet been accepted (14), but it is unquestionably right (47). Richarz and Lonnes (35) obtained an 88 per cent current efficiency for hydrogen peroxide exclusive of what had been lost by catalytic decomposition. Quite recently Fisher and Krönig (7) have obtained a 93.5 per cent current efficiency under favorable conditions. It seems to be practically certain that 100 per cent current efficiency would be obtained if catalytic decomposition could be avoided.

Another argument in favor of this is that the decomposition–voltage curve for sodium peroxide between platinum electrodes is of the same type as that for copper sulfate between copper electrodes, an approximately straight line starting from the origin. This means that the reactions at the two electrodes are the same in fact but opposite in sign.

Consequently the value of $E_h = +1.16 \pm 0.03$ volts must be very close to the true value for the reaction $H_2 + O_2 = H_2O_2$ in a suitably acid solution. It would be more difficult to prove that $E_h = +0.30 \pm 0.02$ volt is approximately the true value for alkaline solutions because of the higher rate of catalytic decomposition of hydrogen peroxide in alkaline solutions. This is not necessary, however, because the close agreement between the chemical and electrical results in acid solution establishes the validity of the chemical method.

Fredenhagen (12) objected to Haber's calling hydrogen peroxide a reducing agent, because Fredenhagen found that hydrogen peroxide oxidizes ferrous chloride completely, even though the measured electromotive force of a hydrogen peroxide electrode relative to the ferro–ferric electrode is the same as that of an acidified solution containing about 10 per cent molar ferrous chloride and 90 per cent molar ferric chloride. There are two mistakes here. The true electromotive force of a hydrogen peroxide electrode is larger than that of a ferric chloride solution, and consequently hydrogen peroxide should oxidize ferrous chloride completely. Also, if Fredenhagen had made up a cell Pt|10 per cent H_2O_2 in $N/10$ HCl|N $FeCl_3$ in $N/10$ HCl|Pt, he would have observed a reduction of ferric chloride in the cell, as we did.

Ferrous salts combine with α,α'-dipyridyl (19) to give complexes in which the concentration of ferrous ions is apparently vanishingly small. This makes the ferric salt a stronger oxidizing agent; consequently it is not surprising that hydrogen peroxide reduces ferric salts quantitatively in presence of α,α'-dipyridyl. As we had none of this substance, we could not make any electromotive force measurements, but they would undoubtedly have fallen in line. It has long been known that hydrogen peroxide in alkaline solutions reduces potassium ferricyanide to potassium ferrocyanide. All who have measured the electromotive force of this reaction have found it come out as it should relatively to our value for hydrogen peroxide.

Since the formation of hydrogen peroxide is the primary reaction in the oxyhydrogen gas cell, it must take 2 faradays to form one gram-molecular weight of hydrogen peroxide. Consequently the oxygen anion concerned must be O_2'', corresponding to the mercurous cation $Hg_2^{\cdot\cdot}$. This is in accord with the experiments of Tanatar (46), who determined the volumes of oxygen set free at the anode from certain hydrogen peroxide solutions and those set free in a sulfuric acid coulometer. The conditions could be so adjusted that two volumes of oxygen were set free from hydrogen peroxide as against one volume of oxygen from the coulometer. This was after correcting for oxygen set free in consequence of catalytic decomposition. In an alkaline barium peroxide solution the anion must be bivalent diatomic oxygen.

If we have a case of reversible oxidation and reduction, such as $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$, the extreme values for a practically pure ferrous salt solution and for a practically pure ferric salt solution will be either on the same side of the true hydrogen peroxide potential for that solution or on opposite sides. If both are on the same side, the reaction will run to an end. Hydrogen peroxide oxidizes ferrous salts completely to ferric salts either in acid or in alkaline solutions. Permanganate is reduced completely both in acid and in alkaline solutions. Lead peroxide is reduced completely to lead sulfate in acid solutions, and lead monoxide is oxidized completely to lead dioxide or sodium plumbate in alkaline solutions. Hydriodic acid is oxidized completely to iodine in acid solutions.

If the two extreme values lie on opposite sides of the true electromotive force for hydrogen peroxide in that solution, a state of equilibrium occurs. Liquid bromine with a low concentration of hydrobromic acid gives a value of $E_h = +1.26$ volts and is reduced by hydrogen peroxide. Bromine with a high concentration of hydrobromic acid gives a value of $E_h = +1.09$ volts, and the hydrobromic acid is oxidized by hydrogen peroxide. The zero point at which traces of hydrogen peroxide are in equilibrium with liquid bromine and hydrobromic acid is at about $E_h = +1.16$ volts, apparently between $+1.17$ and $+1.15$.

The conversion of iodine into iodic acid and back is a very good illustration of this. As the literature at present is in a hopelessly confused state, this case brings out the advantage of our viewpoint. Iodine dissolved in *M* sulfuric acid is converted nearly completely into iodic acid. The reverse reaction does not take place to an extent which can be detected by the casual observer. If one adds a little carbon tetrachloride to a solution of iodic acid in 2 normal sulfuric acid before adding the hydrogen peroxide, the existence of an equilibrium will be shown by the development of a pink color in the carbon tetrachloride. Using dilute hydrogen peroxide a pink color develops with $M/2$ and $M/50$ iodic acid but not with $M/200$ iodic acid. When 30 per cent hydrogen peroxide is added, a pink color is obtained even with $M/2000$ iodic acid. This shows again that hydrogen peroxide is a stronger reducing agent in more concentrated solution. If the carbon tetrachloride is added after the hydrogen peroxide has decomposed completely, no pink color is obtained even with $M/2$ iodic acid.

If one adds iodine crystals to a solution of hydrogen peroxide in 2 normal sulfuric acid, the solution does not become colored by the iodine and the oxidation to iodic acid takes place very slowly. This apparent paradox is due to the catalytic decomposition of the hydrogen peroxide at the surface of the iodine crystals. These crystals become coated with a film of oxygen, which protects them pretty well from the solvent action of the solution. The rate of oxidation can be accelerated by stirring the solution vigorously, or by starting with a saturated solution of iodine in carbon tetrachloride and adding excess iodine. The zero point is about $E_h = +1.16$ volts, apparently between $+1.17$ and $+1.15$.

Auger (1) obtained visible amounts of iodine by starting with a dilute iodic acid solution. We have improved on that technique by starting with a concentrated potassium iodate solution, adding a few drops of hydrochloric acid or sulfuric acid, and then adding 30 per cent hydrogen peroxide. A heavy precipitation of iodine occurs, which stops when the solution becomes neutralized. Further addition of hydrochloric acid causes additional precipitation of iodine. If concentrated hydrochloric acid is added, the iodine is oxidized to iodic acid by the hydrogen peroxide. If caustic potash is then added, iodine will come down again on addition of hydrogen peroxide, provided the solution has not become too dilute. This makes a very striking lecture experiment.

In our experiments the change from reduction to oxidation occurs at about pH = 1.2 to 1.4, apparently regardless of whether one uses hydrochloric acid or sulfuric acid. If one adds the acid in several portions, each one after the preceding portion has been neutralized, one can get a good deal of reduction. If the same amount of acid is added all at once, the pH drops below 1.2 and there is practically no reduction. Since the change occurs at approximately the same pH both with hydrochloric acid and with sulfuric acid, the intermediate formation of iodine monochloride or trichloride cannot be of vital importance as Auger assumed it to be.

The electromotive force measurements on periodic acid and potassium periodate confirm the chemical findings by Tanatar (45) that hydrogen peroxide reduces periodic acid and sodium periodate to iodic acid and sodium iodate, respectively. With potassium iodide and potassium iodate we ran into a serious difficulty which we had not foreseen, although perhaps we should have. The electromotive force of $E_h = +0.16$ should mean that sodium peroxide oxidizes alkaline potassium iodide to potassium iodate. In spite of all our efforts to the contrary, we were forced to confirm the results of our predecessors that sodium peroxide produces practically no potassium iodide from potassium iodate.

A way out of this impossible situation was found at last. One can obtain an electromotive force measurement for sodium sulfite as a reducing agent and one can oxidize sodium sulfite to sodium sulfate; but one cannot reduce sodium sulfate to sodium sulfite. In the presence therefore of a suitable reducing agent, both sodium sulfite and sodium sulfate would be practically stable. The conversion of sodium iodide to sodium iodate is not quite a parallel case to that of sodium sulfate to sodium sulfite, because a sufficiently strong oxidizing agent, such as ozone, will oxidize alkaline sodium iodide to sodium iodate (20) and even to sodium periodate (36). We have found that alkaline permanganate is bleached by alkaline sodium iodide. The difficulty with the hydrogen peroxide is that potassium hypoiodite is the first stage in the oxidation of iodide, and that hydrogen peroxide reduces hypoiodite. To oxidize alkaline potassium iodide to iodate, one must use an oxidizing agent, such as ozone or alkaline permanganate, with a higher oxidizing potential than alkaline potassium hypoiodite. On the reduction side there is no difficulty. Either an alkaline hydrazine or hydroxylamine solution will reduce alkaline potassium iodate to iodide. The reason that hydrogen peroxide can oxidize hydriodic acid to iodic acid is that the first stage is the oxidation to iodine. A strong enough oxidizing agent should oxidize alkaline sodium chloride to sodium hypochlorite and sodium chlorate. Alkaline permanganate will not do it, and we have not tried ozone. Fluorine will do it.

We can now consider the problem of where the oxygen gas comes from when hydrogen peroxide reacts with lead peroxide in sulfuric acid solution. This is simpler than the case of permanganate, and just as typical. There are many differences in detail, but, speaking broadly, there are two schools of thought. One school—led originally by Schönbein, Brodie, and Berthelot—believes that half the oxygen gas comes from the lead peroxide and half from the hydrogen peroxide. The other school—led originally by Weltzien, Traube, and Baeyer—believes that all the oxygen gas comes from the hydrogen peroxide and none of it from the lead peroxide.

Most textbooks adopt the first view—that of Schönbein, Brodie and Berthelot—for no apparent reason. Roscoe and Schorlemmer (38) say: "The oxides of metals such as gold, silver, and platinum immediately cause decomposition of hydrogen dioxide into water and oxygen even in dilute aqueous solutions, and the oxides themselves are simultaneously reduced to the metallic state, the reduction with silver oxide being represented by the equation:

$$\mathrm{Ag_2O + H_2O_2 = 2Ag + H_2O + O_2}$$

"We have here the remarkable phenomenon of a powerful oxidizing agent exerting a reducing action on metallic oxides with formation of the metal. The explanation of this fact is, however, not far to seek. The above-named metals only combine somewhat feebly with oxygen, and their oxides decompose easily into the elements. When they are brought into contact with hydrogen dioxide, which contains one atom of oxygen but feebly united, mutual reduction takes place, the one atom of oxygen in the dioxide combining with one atom of oxygen in the metallic oxide to form a molecule of free oxygen."

If we ear-mark the oxygen which is to go off as gas by italicizing it, we can make clear the difference between the two points of view. According to Roscoe and Schorlemmer one should write the equation:

$$\mathrm{Ag_2}O + \mathrm{H_2O}\cdot O = \mathrm{2Hg} + \mathrm{H_2O} + O_2 \text{ (alkaline)}$$

and

$$\mathrm{PbO}\cdot O + \mathrm{H_2O}\cdot O = \mathrm{PbO} + \mathrm{H_2O} + O_2 \text{ (acid)}$$

According to the other view, which we endorse, one should write:

$$\mathrm{Ag_2O} + \mathrm{H_2}O_2 = \mathrm{2Ag} + \mathrm{H_2O} + O_2 \text{ (alkaline)}$$

and

$$\mathrm{PbO_2} + \mathrm{H_2}O_2 = \mathrm{PbO} + \mathrm{H_2O} + O_2 \text{ (acid)}$$

The oxidation—not reduction—of hydrogen peroxide by ozone should be written:

$$\mathrm{H_2}O_2 + O_2\mathrm{O} = \mathrm{H_2O} + 2O_2$$

We will now give the reasons (39) for adopting the view put forward by Weltzien, Traube, and Baeyer. Hydrogen peroxide may be considered as dissociating reversibly to a very slight extent into monatomic, electrically neutral hydrogen and activated diatomic oxygen: $\mathrm{H_2O_2 \rightleftharpoons 2H + O\cdot O}$. Reductions are effected by the monatomic hydrogen and oxidations by the activated diatomic oxygen, which differs from molecular oxygen by only having one bond between the oxygens. It is an unsaturated oxygen molecule.

If we arrange a cell, Pt | H_2O_2 in H_2SO_4 | H_2SO_4, PbO_2 | Pb, the current will flow from left to right through the cell, lead peroxide will be reduced to lead sulfate at the cathode, and two oxygens will be evolved at the platinum anode for one gram-molecular weight of lead peroxide reduced. The anode reaction is precisely similar to the one studied quantitatively by Tanatar. In this case there can be no question but that the two oxygens come from the hydrogen peroxide and neither one from the lead peroxide. Similar cells can be set up in all cases in which the error in the potential measured at the platinum electrode, due to the difference between the apparent and true electromotive force of hydrogen peroxide or of the reacting substance, is not sufficiently large to obscure things. With platinum in acidified hydrogen peroxide against platinum in acidified permanganate, manganese dioxide, or chromic acid, the peroxide electrode is the anode, as it should be. With platinum in alkaline hydrogen peroxide against platinum in alkaline permanganate, the hydrogen peroxide electrode is the anode, as it should be.

With platinum in alkaline manganous hydroxide against platinum in alkaline hydrogen peroxide, the hydrogen peroxide electrode is the cathode. Theoretically it should be the cathode, when platinum in alkaline lead monoxide is the other electrode; but actually that is not the case. Apparently the reason why this experiment is unsuccessful with normal alkali is that hydrogen peroxide is catalyzed so rapidly by platinum in such a solution that it is impossible to build up the proper potential at the electrode. Once the cause of the trouble was recognized, it was easy to get around the difficulty. Alkaline hydrogen peroxide oxidizes manganous hydroxide to manganese dioxide and is therefore a stronger oxidizing agent than alkaline manganese dioxide. A cell was accordingly made up: Pt | PbO, N KOH | N KOH, MnO_2 | Pt. The manganese dioxide electrode is the cathode; consequently the stronger oxidizing agent, hydrogen dioxide, would also be at the cathode if the catalytic decomposition were eliminated. A similar arrangement made it possible to show that alkaline chromic oxide and alkaline cobaltous oxide are really anodic to hydrogen peroxide of the same general alkalinity.

In every case the current in an electrolytic cell containing hydrogen peroxide flows in the direction predicted by the chemical reaction, or can be made to do so by eliminating the unessential disturbing factors. It is not safe to say that the type of reaction as postulated by Schönbein and Brodie cannot be arranged as an electrolytic cell, but no one has yet done it and it is not clear what would be anode and what cathode. It has also never been explained why hydrogen peroxide and lead peroxide or manganese dioxide should be compatible in alkaline solution and incompatible in acid solution. In the reaction between barium peroxide and iodine, $BaO_2 + I_2 = BaI_2 + O_2$, all the oxygen must come from the peroxide. We may therefore consider the question of the source of the oxygen gas as settled in the way it should have been settled a long time ago—in favor of the view advanced by Weltzien, Traube, and Baeyer. As late as 1858 Schönbein (40) explained the reaction $H_2O_2 + Cl_2 = 2HCl + O_2$ on the basis that chlorine was murium peroxide and not an element.

An additional argument is to be found in the experiments of Fowler and Grant (10) on the effect of heating lead peroxide with potassium chlorate. From Schönbein's point of view the result should have been evolution of oxygen with the formation of lead monoxide and potassium chloride, both substances losing oxygen. Actually there was a nearly quantitative oxidation of potassium chlorate to potassium perchlorate. When dry sodium peroxide is ground with iodine and heated suitably, there is formation of sodium periodate (17).

Raikow (33) takes the ground that a substance cannot have the same formula as a reducing agent and as an oxidizing agent. He therefore considers that the reducing agent is HO—OH and that the oxidizing agent is $H_2{=}O{:}{:}O{=}$. This seems quite unnecessary. We have postulated the reversible dissociation $H_2O_2 \rightleftharpoons 2H + O{-}O$. When hydrogen peroxide acts as a reducing agent, we have 2H reacting with the substance to be reduced and the O—O going off as molecular oxygen. When hydrogen peroxide acts as an oxidizing agent, the activated oxygen reacts both with the substance to be oxidized and with the monatomic hydrogen. For lead oxide in alkaline solution we have, for instance:

$$2H + O{-}O + PbO = H_2O + PbO_2$$

For hydriodic acid in acid solution we have as the first stages:

$$2H + O{-}O + HI = H_2O + HIO$$

Starting with this point of view one cannot admit that the catalytic decomposition of hydrogen peroxide can be represented by the equation $H_2O_2 \rightarrow H_2O + O$. It must be that one molecule of hydrogen peroxide reduces a second one in exactly the same manner that one molecule of hydrogen peroxide reduces one molecule of lead peroxide. The equation would be written:

$$H_2\mathit{O}_2 + H_2O_2 = 2H_2O + \mathit{O}_2$$

After this conclusion had been reached independently, it was a great pleasure to find that Wieland (51) had said the same thing more than a dozen years ago. He considers that the first stage in the catalytic decomposition is the dehydrogenation of one molecule, the hydrogen from which reacts very rapidly with a second molecule. Wieland writes the equations:

$$HO{\cdot}OH \rightarrow O{:}O + 2H$$
$$HO{\cdot}OH + 2H \rightarrow 2H_2O$$

The only difference between Wieland's point of view and ours is that we postulate a reversible dissociation and consequently the formation of O—O with subsequent formation of molecular oxygen, O:O.

If hydrogen peroxide decomposed, as is usually assumed, according to the equation $H_2O_2 \rightarrow H_2O + O$, it would necessarily be one of the most powerful oxidizing agents, because it would be setting free nascent oxygen which is, next to fluorine, the most powerful oxidizing agent that we have at ordinary temperatures. As a matter of fact this work was started with the idea that one could do chemical electrolyses with hydrogen peroxide nearly as well as with fluorine. That view was given up when it was found experimentally that hydrogen peroxide is a rather weak oxidizing agent. This is quite reasonable now that we see that what is first evolved is O·O and not O. While molecular oxygen is not as effective an oxidizing agent as hydrogen peroxide, because of its inertness, molecular oxygen in contact with platinum is a stronger oxidizing agent than hydrogen peroxide, though not so convenient a one. If one writes hydrogen peroxide with the unsymmetrical formula, one gets into difficulty because the dissociation $H_2O{:}O \rightleftharpoons 2H + O{:}O$ gives molecular oxygen.

The catalytic decomposition by platinum may be written:

$$H_2O_2 + Pt = Pt(2H) + O_2$$
$$H_2O_2 + Pt(2H) = Pt + 2H_2O$$

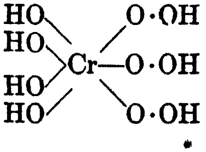
The measured reaction is therefore monomolecular. For this particular case we have practically eliminated the distinction between contact catalysis and reaction catalysis made by Bray (5) and Livingston (22). We do not agree with the conclusions drawn by Bray and Livingston in regard to catalysis in homogeneous solutions, though their premises are right. They have shown "that in acid solution hydrogen peroxide oxidizes bromide to bromine, and reduces bromine to bromide, and that these two reactions can take place independently in the same solution. When the rates of these two compensating reactions are equal, the net result is the catalytic decomposition of hydrogen peroxide. This constitutes a 'steady state,' in which the concentrations of bromine, bromide, and acid remain constant in a single experiment."

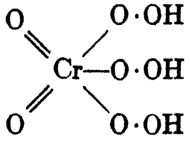
Bray postulates two electromotive forces for molal hydrogen peroxide in molal acid, a reducing one of $E_h = +0.56$ volt and an oxidizing one of $E_h = +1.78$ volts. He considers that an oxidation-reduction catalysis of hydrogen peroxide occurs when the electromotive forces of the oxidation-reduction couple lie between these two limiting values. In the first place, the steady state is not really one, because the concentrations vary with the concentration of hydrogen peroxide. If the catalysis is to continue until all the hydrogen peroxide is used up, the final electromotive force involved is ours of $E_h = +1.16$ volts and not the hypothetical ones given by Bray.

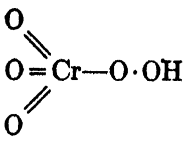
What Bray should have said is that one gets an oxidation-reduction catalysis of hydrogen peroxide when one electromotive force lies above $E_h = +1.16$ volts and the other below it. Bray came to grief with the ferric salt catalysis of hydrogen peroxide, because there is no evidence of any reduction of ferric ion to ferrous ion by hydrogen peroxide. Bray mentions the possibility of oxidation to ferrate, but does not dwell on it. We explain the catalysis by the temporary formation of the instable ferric acid. When neutral hydrogen peroxide is added to neutral ferric chloride solution, a dark red color is formed temporarily, which is undoubtedly due to a higher valence of iron.

This is confirmed by the work of Bohnson (3) and Robertson (37), who photographed the absorption spectra of solutions of ferric chloride alone, barium ferrate dissolved in acetic acid, potassium ferrate, and mixtures of hydrogen peroxide and ferric chloride. There is a striking similarity between the bands for the two ferrates and those for the reaction mixture. On the other hand, a solution of ferric chloride shows no such characteristic bands in the yellow and green, and is totally opaque to the violet. When hydrogen peroxide is added to the ferric chloride, transmission of violet lines takes place and absorption bands appear in the yellow and green.

One of the very interesting things about hydrogen peroxide is the alleged presence of perchromic acid in the blue solution obtained temporarily by adding hydrogen peroxide to a suitably acidified chromic acid solution. It is a regular experiment in all introductory courses in chemistry. As the name "perchromic acid" implies, most people consider that chromium has been oxidized to a higher valence than it has in chromic acid. Friend (13) writes the formulas for the perchromic acids as







giving chromium a valence of seven.

As a matter of fact, the evidence against the existence of a higher oxide of chromium in perchromic acid is conclusive. Chromic acid does not bleach acidified permanganate and is therefore not oxidized by it, although acidified permanganate is a stronger oxidizing agent than chromic acid. The blue compound does bleach acidified permanganate even after the free hydrogen peroxide has been removed.

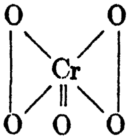
Lead peroxide does not give rise to the blue color. Platinum causes the blue color to fade more rapidly than it would otherwise, but takes quite a while. In spite of this we have been unable to produce the blue oxide by electrolysis with a platinum anode. The only agents which will give rise to the blue color are hydrogen peroxide and compounds which set free hydrogen peroxide, such as ozomolybdic acid, pervanadic acid, pertitanic acid, pertantalic acid, perzirconic acid, peruranic acid, pertungstic acid, perboric acid (8), copper peroxide, mercury peroxide, etc. These are substances whose scientific names do not describe the products. These experiments were done before we had read the paper by Moissan (28), but our line of reasoning is identical with his.

Consequently the blue compound is not a higher oxide of chromium, any more than barium peroxide involves a higher valence of barium. The blue compound is either an addition product or a metathetical product of chromic acid and hydrogen peroxide. It cannot possibly be chromium with a valence of seven, as many people assume. Addition of hydrogen peroxide to a chromic acid electrode does not raise the potential even when a blue color is formed temporarily.

Spitalsky (44) found that in 3 normal sulfuric acid hydrogen peroxide reduces chromic acid practically instantaneously to chromic sulfate. Traube (49) showed that persulfuric acid dissolved in 70 per cent sulfuric acid causes chromic acid to go to chromic sulfate because a sulfuric acid of this concentration converts persulfuric acid rapidly into hydrogen peroxide. With persulfuric acid dissolved in a 40 per cent sulfuric acid no appreciable reduction occurs. This means that persulfuric acid does not oxidize chromic acid to any of the so-called perchromic acids.

There is nothing really new about this. Werther (50), Péchard (30), Melikoff and Pissarjewsky (26), and Pissarjewsky (32) have pointed out more or less clearly that the colored products obtained by adding hydrogen peroxide to acidified chromic acid, vanadic acid, molybdic acid, and tungstic acid do not correspond to higher oxidation stages of these metals.

Schwarz and Giese (43) say that it is very improbable that chromium, which is in the sixth group, should ever have a valence of seven. Also, in all the other cases in which hydrogen peroxide reacts with an acid radical containing a metal, peroxide compounds are formed with an —O:O— group and no increase in the valence of the central atom (pertitanate (2), perzirconate, pervanadate (27), perphosphate, etc.). They come to the conclusion that the so-called perchromic acid is not an acid at all, but a peroxide of the composition CrO_5 and the formula



Over fifty years ago Moissan (28) wrote the formula $CrO_3 \cdot H_2O_2$, which is still good.

Since hydrogen peroxide reduces quadrivalent lead to bivalent lead in acid solutions and reverses this reaction in alkaline solutions, there must be a transition at some point which will not necessarily come at $pH = 7$. Schönbein (37) fixed the point between lead acetate and basic lead acetate. Zotier (52) confirmed this. With neutral lead acetate and hydrogen peroxide he got no lead peroxide; with basic salts he got a slight formation of lead peroxide; and with alkaline solutions he got plenty of lead peroxide. It is not certain just what is meant by basic lead acetate, so we have checked Zotier's results. Addition of hydrogen peroxide to a solution of lead acetate and lead monoxide in the proportions necessary to form $Pb_2(CH_3COO)_3OH$ caused precipitation of lead peroxide. Addition of increasing amounts of 0.766 *N* potassium hydroxide to 5 cc. of a solution of lead acetate (50 g. of $(CH_3COO)_2Pb \cdot 3H_2O$) in 100 cc. of water followed by addition of 5 cc. of a 30 per cent hydrogen peroxide gave the following results. With 1 cc. of potassium hydroxide no lead peroxide. The pH of the solution, as determined by the indicator method, was 6.5. With 2 cc. of potassium hydroxide there was formed lead peroxide. The pH of this solution was 7.0. The zero point for lead acetate to lead peroxide in the presence of potassium hydroxide is between pH 6.5 and 7.0. Substitution of sodium hydroxide does not affect the zero point within these limits of accuracy.

Addition of increasing amounts of $N/100$ acetic acid to 5 cc. of a basic lead acetate solution (10 g. of basic lead acetate, $Pb_2(CH_3COO)_3 \cdot OH$, in 100 cc. of water), followed by addition of 5 cc. of 30 per cent hydrogen peroxide gave the following results. With 35 cc. of acetic acid lead peroxide was still formed, but 40 cc. of acetic acid prevented its formation. The pH values of these solutions were 7.0 and 6.4, respectively. When $N/100$ hydrochloric acid was added, 35 cc. did not prevent the formation of lead peroxide while 40 cc. did. This corresponds to pH values of 6.2 and 5.8, distinctly smaller than the 7.0 and 6.5 found with caustic alkali and acetic acid. This may have been a chloride effect. This seems to have been proved by experiments in which a 1 per cent solution of potassium chloride was substituted more or less completely for the hydrochloric acid. The results in table 3 were obtained for the varying amounts of potassium chloride necessary to prevent the formation of lead peroxide. When only potassium chloride was added to the basic lead acetate, the decrease in pH must have been apparent and not real. The basic lead acetate gives lead peroxide at a platinum anode.

Schönbein (40) reports that hydrogen peroxide reduces alkaline cupric oxide to cuprous oxide, and Brodie (6) says that sodium peroxide oxidizes ammoniacal cupric chloride temporarily to a higher oxide. Both are wrong. Schönbein mistook the yellow of the so-called copper peroxide for the yellow of cuprous oxide. Parnell (29) made the same mistake about ten years later. Brodie did not realize that the so-called copper peroxide is really just that. It does not represent a higher valence for copper, any more than the so-called perchromic acid represents a higher valence of chromium. Cuprous salts are oxidized to cupric salts by hydrogen peroxide both in acid and alkaline solutions just as ferrous salts are oxidized to ferric salts.

TABLE 3

Potassium chloride necessary to prevent the formation of lead peroxide

VOLUME OF KCl (1 PER CENT)	VOLUME OF HCl (*N*/100)	pH
cc.	*cc.*	
0 0	35–40	5 8–6 2
0 7	30–35	6 4
1 0	20–25	6 6
1 5	0	6 4

Curiously enough a somewhat similar mistake has been made with regard to mercuric oxide. Martinon (25) says that mercuric oxide is reduced to black mercurous oxide in alkaline solution by hydrogen peroxide. The electromotive force measurements for Hg | HgO and Pt | HgO contradict this. When pure mercuric oxide is treated with hydrogen peroxide in alkaline solution, it turns black as Martinon says, but the product is not mercurous oxide. By working at 0°C. as Pellini (31) did, one can isolate the red mercury peroxide, which is formed metathetically and which gives a blue solution with chromic acid. On addition of alkali there is an evolution of oxygen and the red compound turns black. That is impure metallic mercury. If it is dissolved in dilute nitric acid, one can then precipitate mercurous chloride, but this is no evidence for the prior existence of mercurous oxide.

It is not really surprising that one cannot measure the true electromotive forces of hydrogen peroxide in acid and in alkaline solutions. One can see the evolution of oxygen as a danger signal. There are other cases where one does not measure the true electromotive forces. Ozone is a stronger oxidizing agent than cobaltic sulfate, but electromotive force measurements do not show it. Luther (24) has given a long list of criteria which should be met before one can postulate that a given electromotive force connotes a given reaction. We do not care for the stipulation that the Peters equation is a necessary criterion. That way leads to the activity concept. Loimaranta (23) cites the cases of trivalent and pentavalent arsenic and trivalent and hexavalent chromic acid where iodine serves profitably as electromotive promoter.

Of especial interest to us is the work of Forbes and Bartlett (9), who found that the apparent electromotive force of acidified chromic acid was raised considerably by addition of ammonium ferrous sulfate. We have confirmed this. With molar chromic acid in molar sulfuric acid an apparent value was obtained of $E_c = +0.990$ volt as given in table 1. On addition of ammonium ferrous sulfate this rose to $E_c = +1.150$ or $E_h = +1.45$ volts. Chromous sulfate, stannous chloride, arsenious acid, and potassium ferrocyanide produce similar though smaller effects.

Forbes and Bartlett at first considered this to be due to a change in the platinum electrode, but pointed out that the effect cannot be obtained with sulfurous acid or with hydrazine. No satisfactory explanation for this phenomenon has yet been given.

Luther (24) obtained a rise of electromotive force by reducing an oxidizing agent instead of oxidizing a reducing agent. A dilute chloric acid has almost no effect on hydrobromic acid. If reduced to chlorine dioxide by means of tetravalent vanadium, the chlorine dioxide oxidizes hydrobromic acid practically instantaneously.

In molar sulfuric acid the apparent electromotive force of hydrogen peroxide increases somewhat with increasing concentration of hydrogen peroxide, whereas the true electromotive force must decrease.

The following general conclusions can be drawn:

1. When the true electromotive force of any oxidizing or reducing agent, with reference to any electrode and in any solution, is larger than the true electromotive force of hydrogen peroxide in the same solution, that substance will be reduced by hydrogen peroxide, provided such a reaction is possible. If the true electromotive force is smaller than the true value for hydrogen peroxide, that substance will be oxidized by hydrogen peroxide, provided such a reaction is possible.

2. The true electromotive force, relatively to the hydrogen electrode, of hydrogen peroxide in *M* hydrochloric or sulfuric acid is about $+1.16 \pm 0.03$ volts; the corresponding value in *M* potassium hydroxide is about $+0.30 \pm 0.02$ volt, subject to a correction for diffusion potential. The zero points for iodine to iodic acid in *M* sulfuric acid and for hydrobromic acid to bromine are apparently $E_h = +1.16$ volts.

3. The primary reaction in the oxyhydrogen gas cell is the formation of hydrogen peroxide, as postulated years ago by G. N. Lewis and by Haber.

4. The oxygen anion in hydrogen peroxide is O_2'', as shown by Tanatar.

5. The current–voltage curve for a sodium peroxide solution between platinum electrodes is the same type as that for a copper sulfate solution between copper electrodes.

6. Hydrogen peroxide may be considered as dissociating reversibly into $2H + O \cdot O$. Reduction is done by the two hydrogen atoms and oxidation by the $O \cdot O$. The symmetrical structure for hydrogen peroxide is indicated.

7. In the reaction between hydrogen peroxide and lead peroxide in acid solution, the lead peroxide is reduced by the hydrogen from the hydrogen peroxide, and all the oxygen gas comes from the hydrogen peroxide. This is the view put forward by Weltzien, Traube, and Baeyer.

8. In the catalytic decomposition of hydrogen peroxide the reaction is

$$2H + O \cdot O + H_2O_2 \rightarrow 2H_2O + O_2$$

and not

$$H_2O_2 \rightarrow H_2O + O$$

This is the view advocated by Wieland. In the presence of platinum the reactions may be written

$$H_2O_2 + Pt = Pt(2H) + O_2$$

and

$$H_2O_2 + Pt(2H) = Pt + 2H_2O$$

The measured reaction is therefore monomolecular.

9. Bray should have said that we get an oxidation-reduction catalysis of hydrogen peroxide when one electromotive force is larger than $E_h = +1.16$ volts and one is smaller. He was led astray by Haber's hypothesis of an oxidation value for hydrogen peroxide greater than $E_h = +1.16$ volts.

10. The blue so-called perchromic acid does not contain chromium with a higher valence than six. This is the view upheld by Moissan. The so-called pertungstates, pertantalates, pervanadates, permolybdates, pertitanates, perzirconates, peruranates, perborates, etc., do not contain higher oxides; nor do copper peroxide and mercury peroxide. Acid permanganate is reduced by the blue compound just as it is by hydrogen peroxide. It is not reduced by chromic acid.

11. When a substance is reduced by hydrogen peroxide in strongly acid solution and oxidized in a strongly alkaline solution, or the other way around, there must be an intermediate pH at which neither change takes place for any given concentration of hydrogen peroxide. With lead acetate this point comes between pH = 6.5 and 7.0. Presence of chloride displaces the apparent position of the point.

12. No satisfactory explanation has yet been given for the rise of

electromotive force when ammonium ferrous sulfate, chromous sulfate, stannous chloride, arsenious acid, or potassium ferrocyanide is added to an acidified chromic acid solution.

13. In molar sulfuric acid the apparent electromotive force of hydrogen peroxide increases with increasing concentration of hydrogen peroxide, whereas the true electromotive force must decrease.

14. Hydrogen peroxide reduces acidified potassium iodate to iodine when the pH is larger than about 1.2 to 1.4, and oxidizes iodine to iodic acid when the pH is smaller than that.

15. In approximately molar caustic potash, hydrogen peroxide should apparently oxidize potassium iodide to iodate, but the first step in such an oxidation is the formation of potassium hypoiodite and this substance is reduced by hydrogen peroxide. Consequently both potassium iodide and potassium iodate are practically stable to hydrogen peroxide in alkaline solutions.

16. To oxidize alkaline potassium iodide to iodate, one must use a more powerful oxidizing agent than potassium hypoiodite. Ozone and alkaline permanganate meet this requirement.

17. It is now possible to draw a sharp dividing line between peroxides and dioxides. The term lead peroxide is so well established that it is doubtful whether a change in nomenclature is wise.

18. The chemistry of hydrogen peroxide is a hopeless subject for the phenomenological, or Baconian, experimenter, because the misleading experiment is everywhere.

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PHOTOSYNTHESIS OF FORMALDEHYDE IN TROPICAL SUNLIGHT

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The review of the literature on the subject of photosynthesis, from the advancement of Baeyer's hypothesis as regards assimilation of carbon dioxide up to the position of the work as it stands at the present time, leads one to believe that it demands (a) an investigation of the likely impurities besides organic matter, dust, etc., present at the seat of the evolution of carbon dioxide which is to be exposed to light, and (b) suggestions as to an apparatus which can be used everywhere under identical conditions.

Results obtained in an investigation carried out with a view to find out the likely impurities and to suggest an apparatus, are embodied in the present paper.

EXPERIMENTAL

The experiments were carried out in sunlight using the apparatus shown in figure 1 and also in glass bulbs joined together, as will be described. Figure 1 indicates an apparatus made of soft glass having three bulbs a, b, and c. The bulbs a and b are joined together with a tube which is connected with the delivery tube d through which the liberated carbon dioxide passes into the solution in the bulb c; e is a passage to take out and fill in any solution in the bulb c. The passage e is covered with a test tube containing conductivity water. The bulbs a and b contain the carbonates under conductivity water or in solution, and hydrochloric acid, respectively. The carbonate and the acid are introduced into the bulbs through the mouth f, which is afterwards sealed in a blow-pipe flame. By tilting the apparatus towards the bulb a, the acid in b is allowed to come in contact with the carbonate in a and thus the evolution of carbon dioxide takes place; the gas passes through the delivery tube d into the solution in the bulb c. The acid is poured on the carbonate gradually from day to day while the apparatus is sealed at f and the passage e is covered with conductivity water, which is replaced from time to time, in a test tube. There is no possibility of any organic matter or dust entering the bulbs a, b, and c. Thus the necessity of corks, rubber tubing, or an exit tap-way arrangement can be easily dispensed with.

Another apparatus wherein carbon dioxide, in the presence of water, is to be exposed has two glass bulbs joined together and sealed at the other ends. The bulbs contain carbonate or marble pieces and hydrochloric acid, respectively. The bulb containing the acid is tilted towards the other bulb, and thus the acid is allowed to come in contact with the carbonate or marble pieces, or the carbonate with metallic magnesium or tin foil. Carbon dioxide and hydrogen, thus formed, are in a nascent state and can be conveniently exposed to light at the time of their liberation, in the presence of water.

Before use the apparatus was carefully cleaned with hot chromic acid mixture and washed several times with distilled and finally with conductivity water. Merck's extra pure guaranteed reagents were used after necessary precautions.

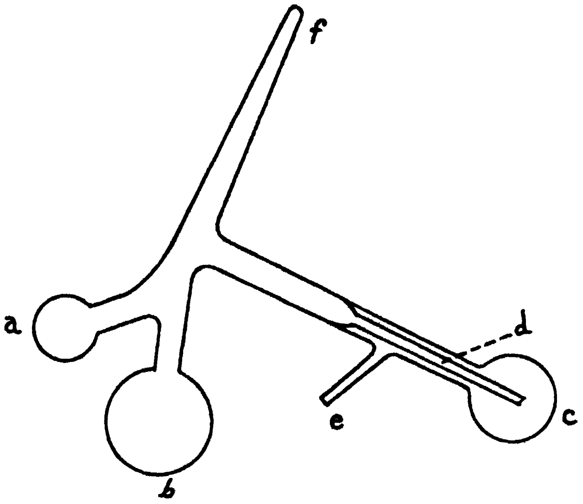

FIG. 1. THE APPARATUS

Schryver's and Rimmi's tests were applied for the detection of formaldehyde. The contents of the apparatus were taken out in beakers after exposure to sunlight, neutralized, and distilled. The distillates were tested for formaldehyde. The marble pieces, barium carbonate, magnesium powder, and carbonates of nickel and cobalt, were well washed with hot conductivity water before use.

DISCUSSION OF RESULTS

The carbon dioxide, obtained from barium or sodium carbonate and hydrochloric acid, though exposed to light for forty-four hours, in the presence of water and in "statu nascendi," does not indicate the formation of formaldehyde. However, if the source of carbon dioxide is changed to marble pieces and hydrochloric acid there is a clear formation of formaldehyde, even for an exposure of eight hours. This must be due to certain impurities present in marble pieces (vide experiments 1, 2, and 3, table 1).

L. Moser (2) has discussed the purification of the carbon dioxide gas

TABLE 1

Experiments performed in the double-bulbed apparatus

EXPT. NO.	CONTENTS OF		TIME OF EXPOSURE	RESULTS
	Bulb 1	Bulb 2		
			hours	
1*	$BaCO_3$ under conductivity water	$N/10$ HCl	44	No formaldehyde detected
2*	10 per cent Na_2CO_3 solution	$N/10$ HCl	44	No formaldehyde detected
·3†	Marble pieces	$N/10$ HCl	8	Small quantities of formaldehyde detected
4†	$BaCO_3$ and Mg powder	$N/10$ HCl	8	Odor of formaldehyde; formaldehyde detected
5†	$BaCO_3$ and Sn foil	$N/10$ HCl	8	Formaldehyde detected; no odor of formaldehyde

* These experiments were repeated four times.

† These experiments were carried out in the dark with negative results.

TABLE 2

Experiments performed in the apparatus shown in figure 1

EXPT. NO.	CONTENTS OF			TIME OF EXPOSURE	RESULTS
	Bulb a	Bulb b	Bulb c		
				hours	
6	$BaCO_3$	$N/10$ HCl	Conductivity water	43	No formaldehyde detected
7	$BaCO_3$	$N/10$ HCl	Dilute solution of $FeCl_3$	44	No formaldehyde detected
8	$BaCO_3$	$N/10$ HCl	$NiCO_3$ suspended under conductivity water	40	No formaldehyde detected
9	Marble pieces	N HCl	Conductivity water	8	Small quantities of formaldehyde detected
10	$BaCO_3$	$N/10$ HCl	Dilute solution of H_2S	8	Small quantities of formaldehyde detected
11	$BaCO_3$	$N/10$ HCl	Dilute solution of H_2SO_3	8	Small quantities of formaldehyde detected
12	$BaCO_3$	$N/10$ HCl	Mg powder suspended under conductivity water	8	Formaldehyde detected; odor of formaldehyde

All of these experiments were carried out in the dark with negative results.

from marble pieces and hydrochloric acid and recommends the use of cupric sulfate on pumice to remove hydrogen sulfide and a solution of potassium permanganate to remove sulfur dioxide. Thus the impurities which are likely to be present and can be removed completely by using such reagents as copper sulfate on pumice and potassium permanganate, are the well-known reducing agents. The presence of these substances at the seat of reaction is responsible for definite tests of the formation of formaldehyde as is indicated by the results of experiments Nos. 3 and 5 (table 1) and Nos. 9, 10, and 11 (table 2). Great care is, therefore, essential to remove the above "impurities" when marble with hydrochloric acid is used as a source of carbon dioxide. It is quite clear from experiments No. 4 and 12 that, by using magnesium powder as a reducing agent, there is a distinct formation of formaldehyde so as to give off its odor even after an exposure of about eight hours to sunlight, while in the dark under the same conditions no formaldehyde is formed. Even Fenton (1) could not get the results so clearly in an ordinary "dark reaction" when a stream of carbon dioxide was passed to saturation for about eighteen to twenty-four hours through pure water in contact with several rods of amalgamated magnesium. He obtained slight indication of formaldehyde formation. It seems that the nascent state of both carbon dioxide and hydrogen is responsible for distinct formation of formaldehyde in the results mentioned above.

Further work has been undertaken to study the effect of different and increased periods of exposure to light by using the above apparatus and purest carbon dioxide.

SUMMARY

1. The experiments carried out reveal that the photoreduction of carbon dioxide to formaldehyde is facilitated by the presence of hydrogen in a nascent state, the nascent state of carbon dioxide being another condition.

2. An apparatus has been suggested wherein both carbon dioxide and hydrogen can be exposed to light at the time of their liberation by avoiding the use of corks, rubber tubing, exit tap-way arrangements, etc., and with the exclusion of organic matter, dust, etc.

3. Impurities which are much discussed in the literature might be hydrogen sulfide and sulfur dioxide in small quantities.

The author gratefully acknowledges the help of his senior colleague, Prof. Chandorkar, with whose skill in glass blowing it was possible to prepare the apparatus.

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THEOREMS CONCERNING THE ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS OF STRONG AND WEAK ELECTROLYTES

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I. INTRODUCTION

From a strictly thermodynamic point of view we may study the properties of solutions of electrolytes by considering the solute as undissociated, completely dissociated, or incompletely dissociated. We thus have three corresponding "descriptions" of the same solution and three sets of activity coefficients. Thermodynamics imposes definite mathematical relations between these various sets. The straightforward derivation of these relations is the purpose of the present paper. We shall make use of the thermodynamic method of Gibbs, as expounded for instance in Guggenheim's (2) recent book or in De Donder's "Affinity" (1). A comparison will be made with the method of Lewis and Randall (4). The results thus obtained are general. They lead to simple formulas for the particular cases of extremely low concentrations and of very weak electrolytes.

II. LIST OF SYMBOLS AND FUNDAMENTAL RELATIONS

T = absolute temperature; P = exterior pressure
Description No. 1: the solute is assumed to be undissociated.

$$\left.\begin{array}{ll}\mu_1^{(1)} & = \text{chemical potential}\\ N_1^{(1)} & = \text{mole fraction}\\ f_1^{(1)} & = \text{activity coefficient}\\ g_1^{(1)} & = \text{osmotic coefficient}\end{array}\right\}\text{ of the solvent.}$$

$$\left.\begin{array}{ll}\mu_2^{(1)} & = \text{chemical potential}\\ N_2^{(1)} & = \text{mole fraction}\\ f_2^{(1)} & = \text{activity coefficient}\end{array}\right\}\text{ of the solute.}$$

m = molality of the solution
M = number of moles corresponding to 1000 g. of solvent (for water M = 55.51).

Between these various quantities the following relations hold:

$$\mu_1^{(1)} = \mu_1^{(1)0}(T, P) + RT \ln N_1^{(1)} f_1^{(1)} \tag{1.1}$$

$$\mu_1^{(1)} = \mu_1^{(1)0}(T, P) + g_1^{(1)} RT \ln N_1^{(1)} \tag{1.2}$$

$$\mu_2^{(1)} = \mu_2^{(1)0}(T, P) + RT \ln N_2^{(1)} f_2^{(1)} \tag{1.3}$$

The μ^0's are for a given solvent functions of temperature and pressure only. We also have:

$$N_1^{(1)} = \frac{M}{m + M} \tag{1.4}$$

$$N_2^{(1)} = \frac{m}{m + M} \tag{1.5}$$

Description No. 2: the solute is regarded as completely dissociated, each molecule breaking up into ν_+ positive ions and ν_- negative ions, the sum $\nu_+ + \nu_-$ being represented by ν.

$$\left.\begin{array}{ll} \mu_1^{(2)} & = \text{chemical potential} \\ N_1^{(2)} & = \text{mole fraction} \\ f_1^{(2)} & = \text{activity coefficient} \\ g_1^{(2)} & = \text{osmotic coefficient} \end{array}\right\} \text{of the solvent.}$$

$$\left.\begin{array}{ll} \mu_+^{(2)}, \mu_-^{(2)} & = \text{chemical potentials} \\ N_+^{(2)}, N_-^{(2)} & = \text{mole fractions} \\ f_+^{(2)}, f_-^{(2)} & = \text{activity coefficients} \end{array}\right\} \text{of the positive and negative ions.}$$

We have:

$$\mu_1^{(2)} = \mu_1^{(2)0}(T, P) + RT \ln N_1^{(2)} f_1^{(2)} \tag{2.1}$$

$$\mu_1^{(2)} = \mu_1^{(2)0}(T, P) + g_1^{(2)} RT \ln N_1^{(2)} \tag{2.2}$$

$$\mu_+^{(2)} = \mu_+^{(2)0}(T, P) + RT \ln N_+^{(2)} f_+^{(2)} \tag{2.3}$$

$$\mu_-^{(2)} = \mu_-^{(2)0}(T, P) + RT \ln N_-^{(2)} f_-^{(2)} \tag{2.4}$$

$$N_1^{(2)} = \frac{M}{\nu m + M} \tag{2.5}$$

$$N_+^{(2)} = \frac{\nu_+ m}{\nu m + M} \tag{2.6}$$

$$N_-^{(2)} = \frac{\nu_- m}{\nu m + M} \tag{2.7}$$

Description No. 3: the solute is regarded as incompletely dissociated into single ions, the molality of the undissociated solute being $(1 - \alpha)m$, that of the positive ion $\alpha\nu_+ m$, and that of the negative ion $\alpha\nu_- m$. A more detailed treatment could take into account the possible presence of intermediate and complex ions.

$$\left.\begin{array}{ll}\mu_1^{(3)} & = \text{chemical potential}\\ N_1^{(3)} & = \text{mole fraction}\\ f_1^{(3)} & = \text{activity coefficient}\\ g_1^{(3)} & = \text{osmotic coefficient}\end{array}\right\}\text{ of the solvent.}$$

$$\left.\begin{array}{ll}\mu_+^{(3)},\ \mu_-^{(3)} & = \text{chemical potentials}\\ N_+^{(3)},\ N_-^{(3)} & = \text{mole fractions}\\ f_+^{(3)},\ f_-^{(3)} & = \text{activity coefficients}\end{array}\right\}\text{ of the positive and negative ions.}$$

$$\left.\begin{array}{ll}\mu_u^{(3)} & = \text{chemical potential}\\ N_u^{(3)} & = \text{mole fraction}\\ f_u^{(3)} & = \text{activity coefficient}\end{array}\right\}\text{ of the undissociated solute.}$$

We have:

$$\mu_1^{(3)} = \mu_1^{(3)0}(T, P) + RT \ln N_1^{(3)} f_1^{(3)} \tag{3.1}$$

$$\mu_1^{(3)} = \mu_1^{(3)0}(T, P) + g_1^{(3)} RT \ln N_1^{(3)} \tag{3.2}$$

$$\mu_+^{(3)} = \mu_+^{(3)0}(T, P) + RT \ln N_+^{(3)} f_+^{(3)} \tag{3.3}$$

$$\mu_-^{(3)} = \mu_-^{(3)0}(T, P) + RT \ln N_-^{(3)} f_-^{(3)} \tag{3.4}$$

$$\mu_u^{(3)} = \mu_u^{(3)0}(T, P) + RT \ln N_u^{(3)} f_u^{(3)} \tag{3.5}$$

$$N_1^{(3)} = \frac{M}{[1 + (\nu - 1)\alpha]m + M} \tag{3.6}$$

$$N_+^{(3)} = \frac{\alpha\nu_+ m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.7}$$

$$N_-^{(3)} = \frac{\alpha\nu_- m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.8}$$

$$N_u^{(3)} = \frac{(1 - \alpha)m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.9}$$

Since the μ^0's are independent of composition, it is evident that they are related as follows:

$$\mu_1^{(1)0} = \mu_1^{(2)0} = \mu_1^{(3)0} \tag{4.1}$$

$$\mu_+^{(2)0} = \mu_+^{(3)0} \tag{4.2}$$

$$\mu_-^{(2)0} = \mu_-^{(3)0} \tag{4.3}$$

$$\mu_2^{(1)0} = \mu_u^{(3)0} \tag{4.4}$$

III. FREE ENERGY OF THE SOLUTION IN THE THREE "DESCRIPTIONS"

Let us apply the well-known relation between the free energy, F, the chemical potentials, μ_i, and the numbers of moles, n_i, of the various constituents:

$$F = \sum_i \mu_i n_i \tag{5}$$

The free energy of an amount of solution consisting of 1000 g. of solvent and m moles of electrolyte is given in description No. 1 by

$$F = M\mu_1^{(1)} + m\mu_2^{(1)} \tag{6.1}$$

in description No. 2 by

$$F = M\mu_1^{(2)} + m(\nu_+\mu_+^{(2)} + \nu_-\mu_-^{(2)}) \tag{6.2}$$

in description No. 3 by

$$F = M\mu_1^{(3)} + m[\alpha(\nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)}) + (1-\alpha)\mu_u^{(3)}] \tag{6.3}$$

These three expressions of F for the same solution should of course be identical. Moreover, the contribution of the solvent is the same in the three cases, as well as that of the solute. Equations 6.1, 6.2, and 6.3 give then:

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} \tag{7.1}$$

and

$$\mu_2^{(1)} = \nu_+\mu_+^{(2)} + \nu_-\mu_-^{(2)} = \alpha(\nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)}) + (1-\alpha)\mu_u^{(3)} \tag{7.2}$$

IV. ACTIVITY AND OSMOTIC COEFFICIENTS OF THE SOLVENT

A. Relations between the three activity coefficients of the solvent

From equations 7.1, 4.1, 1.1, 2.1, and 3.1 we deduce

$$N_1^{(1)}f_1^{(1)} = N_1^{(2)}f_1^{(2)} = N_1^{(3)}f_1^{(3)} \tag{8}$$

and, thanks to equations 1.4, 2.4, and 3.6,

$$\frac{f_1^{(1)}}{m+M} = \frac{f_1^{(2)}}{\nu m + M} = \frac{f_1^{(3)}}{[1+(\nu-1)\alpha]m + M} \tag{9}$$

B. Relations between the three osmotic coefficients of the solvent

Thanks to equations 1.2, 2.2, and 3.2, equation 8 also gives:

$$g_1^{(1)} \ln N_1^{(1)} = g_1^{(2)} \ln N_1^{(2)} = g_1^{(3)} \ln N_1^{(3)} \tag{10.1}$$

$$g_1^{(1)} \ln\left(1 + \frac{m}{M}\right) = g_1^{(2)} \ln\left(1 + \frac{\nu m}{M}\right) = g_1^{(3)} \ln\left[1 + \frac{\{1+(\nu-1)\alpha\}m}{M}\right] \tag{10.2}$$

C. Special case of extremely dilute solutions

m, νm, $[1 + (\nu - 1)\alpha]m$ are then negligible compared to M. Equations 9 and 10.2 become

$$f_1^{(1)} = f_1^{(2)} = f_1^{(3)} \tag{11}$$

$$g_1^{(1)} = \nu g_1^{(2)} = [1 + (\nu - 1)\alpha]g_1^{(3)} \tag{12}$$

V. RELATIONS BETWEEN THE SETS OF ACTIVITY COEFFICIENTS OF THE SOLUTE

A. General relations

In description No. 3 the ions are regarded as being in equilibrium with the undissociated part of the solute. We thus have the equilibrium condition:

$$\mu_u^{(3)} = \nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)} \tag{13}$$

Equation 7.2 can then be written:

$$\mu_2^{(1)} = \nu_+\mu_+^{(2)} + \nu_-\mu_-^{(2)} = \nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)} = \mu_u^{(3)} \tag{14}$$

From this relation and from equations 1.3, 2.3, 2.4, 3.3, 3.4, and 3.5, modified on account of equations 4.1, 4.2, 4.3, and 4.4, we deduce:

$$\begin{aligned} &\ln [N_2^{(1)}f_2^{(1)}] + \frac{\mu_2^{(1)0} - \nu_+\mu_+^{(2)0} - \nu_-\mu_-^{(2)0}}{RT} \\ &= \ln [(N_+^{(2)})^{\nu_+}(N_-^{(2)})^{\nu}\ (f_+^{(2)})^{\nu_+}(f_-^{(2)})^{\nu_-}] = \ln [(N_+^{(3)})^{\nu_+}(N_-^{(3)})^{\nu_-}(f_+^{(3)})^{\nu_+}(f_-^{(3)})^{\nu_-}] \\ &= \ln [N_u^{(3)}f_u^{(3)}] + \frac{\mu_2^{(1)0} - \nu_+\mu_+^{(2)0} - \nu_-\mu_-^{(2)0}}{RT} \end{aligned} \tag{15}$$

Introducing the equilibrium constant K (T, P) defined by

$$\ln [K(T, P)] = \frac{\mu_u^{(3)0} - \nu_+\mu_+^{(3)0} - \nu_-\mu_-^{(3)0}}{RT} = \frac{\mu_2^{(1)0} - \nu_+\mu_+^{(2)0} - \nu_-\mu_-^{(2)0}}{RT} \tag{16}$$

equation 15 becomes

$$\begin{aligned} KN_2^{(1)}f_2^{(1)} &= (N_2^{(2)})^{\nu_+}(N_-^{(2)})^{\nu}\ (f_+^{(2)})^{\nu_+}(f_-^{(2)})^{\nu_-} \\ &= (N_+^{(3)})^{\nu_+}(N_-^{(3)})^{\nu_-}(f_+^{(3)})^{\nu_+}(f_-^{(3)})^{\nu_-} = KN_u^{(3)}f_u^{(3)} \end{aligned} \tag{17}$$

It has been pointed out by Guggenheim (3) that ionic activity coefficients are thermodynamically undetermined. Thermodynamically determined are only combinations of ionic activity coefficients of the form

$$\prod_i f_i^{\lambda_i} \tag{18.1}$$

in which the quantities λ_i are related to the algebraic valences z_i of the ions by the relation:

$$\sum_i \lambda_i z_i = 0 \tag{18.2}$$

In the case of a single electrolyte an expression of the form of equation 18.1 is the mean activity coefficient of the ions $f_\pm$ defined by

$$(f_\pm)^\nu = (f_+)^{\nu_+}(f_-)^{\nu_-} \tag{19}$$

It has thermodynamic significance because

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{20}$$

It is also convenient to define mean mole fractions $N_\pm$

$$(N_\pm)^\nu = (N_+)^{\nu_+}(N_-)^{\nu_-} \tag{21}$$

and mean molalities

$$(m_\pm)^\nu = (m_+)^{\nu_+}(m_-)^{\nu_-} = \nu_+^{\nu_+}\nu_-^{\nu_-}\cdot m^\nu \tag{22}$$

These mean quantities (19, 21, and 22) may be used both in description 2 and in description 3.

Equation 17 then becomes

$$KN_2^{(1)}f_2^{(1)} = [N_\pm^{(2)}f_\pm^{(2)}]^\nu = [N_\pm^{(3)}f_\pm^{(3)}]^\nu = KN_u^{(3)}f_u^{(3)} \tag{23}$$

or, thanks to equations 1.5, 1.6, 2.6, 2.7, 3.7, 3.8, and 3.9 ,

$$K\frac{m}{m+M}f_2^{(1)} = \left[\frac{m_\pm^{(2)}f_\pm^{(2)}}{\nu m+M}\right]^\nu = \left[\frac{m_\pm^{(3)}f_\pm^{(3)}}{\{1+(\nu-1)\alpha\}m+M}\right]^\nu$$

$$= K\frac{m_u^{(3)}}{[1+(\nu-1)\alpha]m+M}\cdot f_u^{(3)} \tag{24}$$

Equation 23 could be decomposed into the two symmetrical relations:

$$N_2^{(1)}f_2^{(1)} = N_u^{(3)}f_u^{(3)} \tag{25.1}$$

$$N_\pm^{(2)}f_\pm^{(2)} = N_\pm^{(3)}f_\pm^{(3)} \tag{25.2}$$

The corresponding relations deduced from equation 24 are less symmetrical:

$$\frac{mf_2^{(1)}}{m+M} = \frac{m_u^{(3)}f_u^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{26.1}$$

$$\frac{m_\pm^{(2)}f_\pm^{(2)}}{\nu m+M} = \frac{m_\pm^{(3)}f_\pm^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{26.2}$$

We have

$$m_u^{(3)} = (1-\alpha)m \tag{27.1}$$

$$m_\pm^{(3)} = \alpha m_\pm^{(2)} \tag{27.2}$$

Equations 26.1 and 26.2 become:

$$\frac{f_2^{(1)}}{m + M} = \frac{(1 - \alpha)f_u^{(3)}}{[1 + (\nu - 1)\alpha]m + M} \tag{28.1}$$

$$\frac{f_\pm^{(2)}}{\nu m + M} = \frac{\alpha f_\pm^{(3)}}{[1 + (\nu - 1)\alpha]m + M} \tag{28.2}$$

B. Special case of extremely dilute solutions

When m, νm, $[1 + (\nu - 1)\alpha]m$ are negligible compared to M, equations 12, 23.1, and 23.2 become:

$$K\frac{m}{M}f_2^{(1)} = \left[\frac{m_\pm^{(2)}f_\pm^{(2)}}{M}\right]^\nu = \left[\frac{m_\pm^{(3)}f_\pm^{(3)}}{M}\right]^\nu = K\frac{m_u}{M}f_u^{(3)} \tag{29}$$

$$f_2^{(1)} = (1 - \alpha)f_u^{(3)} \tag{30.1}$$

$$f_\pm^{(2)} = \alpha f_\pm^{(3)} \tag{30.2}$$

These equations are approximate but general, since they do not involve non-thermodynamic assumptions.

VI. THE LIMITING VALUES OF THE ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS AT INFINITE DILUTION

The coefficients

$$f_1^{(1)},\ f_1^{(2)},\ f_1^{(3)}$$
$$g_1^{(1)},\ g_1^{(2)},\ g_1^{(3)}$$
$$f_2^{(1)},\ f_\pm^{(2)},\ f_\pm^{(3)},\ f_u^{(3)}$$

are all thermodynamically indeterminate when m tends towards 0. It is necessary, in order to determine them all, to make non-thermodynamic assumptions regarding: (a) the limiting values for $m = 0$ in one of the descriptions, and (b) the behavior of the function $\alpha = \alpha(m)$ as m approaches 0. We shall assume that the solution becomes ideal in description No. 2 when m tends towards 0. We thus have:

$$[\lim f_1^{(2)}]_{m=0} = 1 \tag{31.1}$$

$$[\lim g_1^{(2)}]_{m=0} = 1 \tag{31.2}$$

$$[\lim f_\pm^{(2)}]_{m=0} = 1 \tag{31.3}$$

Moreover we shall assume that

$$[\lim \alpha]_{m=0} = 1 \tag{31.4}$$

regardless of the actual form of the function $\alpha = \alpha(m)$. We then deduce from equation 11 (the formulas obtained above for small molalities become more and more accurate as m tends towards 0):

$$\lim f_1^{(1)} = \lim f_1^{(2)} = \lim f_1^{(3)} = 1 \tag{32}$$

From equation 12

$$\lim g_1^{(1)} = \nu \lim g_1^{(2)} = \nu \tag{33.1}$$

$$\lim g_1^{(3)} = \lim g_1^{(2)} = 1 \tag{33.2}$$

From equations 29 and 22:

$$\lim f_2^{(1)} = \frac{\nu_+^{\nu_+} \nu_-^{\nu_-}}{K} \lim \left(\frac{m}{M}\right)^{\nu-1} (f_\pm^{(2)})^\nu = 0 \tag{34.1}$$

or

$$\lim f_2^{(1)} = 0 \tag{34.2}$$

From equation 30.1:

$$\lim f_u^{(3)} = \lim \frac{f_2^{(1)}}{1 - \alpha} \tag{35}$$

Since $\lim f_2^{(1)} = 0$ and $\lim (1 - \alpha) = 0$, $f_u^{(3)}$ is indeterminate. From equation 30.2

$$\lim f_\pm^{(3)} = \lim \frac{f_\pm^{(2)}}{\alpha} = 1 \tag{36}$$

VII. PARTICULAR CASE OF VERY WEAK ELECTROLYTES

Instead of making use of the assumptions 31.1, 31.2, and 31.3 of the foregoing section, it will be more convenient, in the case of very weak electrolytes, to assume that:

$$[\lim f_1^{(3)}]_{m=0} = 1 \tag{37.1}$$

$$[\lim g_1^{(3)}]_{m=0} = 1 \tag{37.2}$$

$$[\lim f_\pm^{(3)}]_{m=0} = 1 \tag{37.3}$$

$$[\lim f_u^{(3)}]_{m=0} = 1 \tag{37.4}$$

$$[\lim \alpha]_{m=0} = 1 \tag{37.5}$$

If the electrolyte is so weak that $f_u^{(3)}$ and $f_\pm^{(3)}$ approach unity much more rapidly than α, equations 30.1 and 30.2 become:

$$f_2^{(1)} = 1 - \alpha \tag{38.1}$$

$$f_\pm^{(2)} = \alpha \tag{38.2}$$

These relations, approximately valid for small molalities, are thus partly non-thermodynamic.

For electrolytes obeying exactly Ostwald's dilution law:

$$\frac{\alpha^{\nu} m^{\nu-1}}{1-\alpha} = K \tag{39}$$

we may replace our assumptions (37) by:

$$f_1^{(3)} = 1 \tag{40.1}$$

$$g_1^{(3)} = 1 \tag{40.2}$$

$$(f_{\pm}^{(3)})^{\nu} = f_u^{(3)} \tag{40.3}$$

relations holding in the same range of extreme dilutions as the dilution law (39).

Equation 38.2 is a justification for referring, as is often done, to $f_{\pm}^{(2)}$ as to a "thermodynamic degree of dissociation." The considerations developed in the present paper should clearly indicate the limitations of this concept (5).

VIII. COMPARISON WITH THE METHOD OF LEWIS AND RANDALL

The activity a_2 and the activity coefficient γ_2 of a solute species are defined by Lewis and Randall (reference 4, p. 255) as follows:

$$F - F^0 = RT \ln a_2 = RT \ln (m\gamma_2) \tag{41}$$

F and F^0 are molal free energies. The superscript 0 refers to a "standard state." For given temperature and pressure F^0 is independent of composition. It is moreover assumed that

$$(\lim \gamma_2)_{m\to 0} = 1 \tag{42}$$

In the notation of the present paper equation 41 would read:

$$\mu_2^{(1)} = \mu_2^{(1)0\prime}\ (T, P) + RT \ln (m\gamma_2^{(1)}) \tag{43}$$

From equations 1.3 and 1.5 we deduce:

$$\mu_2^{(1)} = \mu_2^{(1)0} + RT \ln \left[\frac{mf_2^{(1)}}{m+M}\right] = \mu_2^{(1)0} - RT \ln M + RT \ln \left[\frac{mf_2^{(1)}}{1+\frac{m}{M}}\right] \tag{44}$$

Comparing equations 43 and 44 we get:

$$\mu_2^{(1)0\prime} = \mu_2^{(1)0} - RT \ln M \tag{45}$$

and

$$\gamma_2^{(1)} = \frac{f_2^{(1)}}{1+\frac{m}{M}} \tag{46}$$

or, in terms of the mole fraction $N_1^{(1)}$ of the solvent,

$$\gamma_2^{(1)} = f_2^{(1)} \cdot N_1^{(1)} \tag{47}$$

The activity coefficients γ of Lewis and Randall coincide with the "rational" activity coefficients f only at very low concentrations. From equation 47 we see that, even for ideal solutions, γ_2 will be appreciably different from unity at high concentrations. In the same way we have in description No. 2:

$$\gamma_\pm^{(2)} = \frac{f_\pm^{(2)}}{1 + \dfrac{\nu m}{M}} \tag{48}$$

and in description No. 3:

$$\gamma_\pm^{(3)} = \frac{f_\pm^{(3)}}{1 + [1 + (\nu - 1)\alpha]\dfrac{m}{M}} \tag{49.1}$$

$$\gamma_u^{(3)} = \frac{f_u^{(3)}}{1 + [1 + (\nu - 1)\alpha]\dfrac{m}{M}} \tag{49.2}$$

Replacing the various f's by the various γ's in equation 24 we obtain, thanks to equations 46, 48, 49.1, and 49.2,

$$K\frac{m}{M}\gamma_2^{(1)} = \left[\frac{m_\pm^{(2)}\gamma_\pm^{(2)}}{M}\right]^\nu = \left[\frac{m_\pm^{(3)}\gamma_\pm^{(3)}}{M}\right]^\nu = K\frac{m_u^{(3)}}{M}\gamma_u^{(3)} \tag{50}$$

a remarkably symmetrical relation.

In terms of activities we then have

$$K\frac{a_2^{(1)}}{M} = \frac{(a_+^{(2)})^{\nu_+}(a_-^{(2)})^{\nu_-}}{M^\nu} \tag{51}$$

or

$$\frac{(a_+^{(2)})^{\nu_+}(a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = KM^{\nu-1} = K' \tag{52}$$

As shown before (equation 16), K is the true "dissociation constant" of the electrolyte. It is hence not allowed by thermodynamics to assume arbitrarily, as do Lewis and Randall at the starting point of their treatment of strong electrolytes (reference 4, p. 326), that

$$\frac{(a_+^{(2)})^{\nu_+}(a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = 1 \tag{53}$$

Fortunately this relation is never used, the significant relations being:

$$(a_+^{(2)})^{\nu_+} (a_-^{(2)})^{\nu_-} = (a_\pm^{(2)})^{\nu} \tag{54}$$

and

$$(\gamma_+^{(2)})^{\nu_+} (\gamma_-^{(2)})^{\nu_-} = (\gamma_\pm^{(2)})^{\nu} \tag{55}$$

which are in no way expressions of the law of mass action. Equation 52 is the mathematical formulation of a "comparison" between descriptions 1 and 2.

As long as no use is made of the third description, assumption 53, although unnecessary, is perhaps permissible but, on the other hand, when all the descriptions are used (cf. Randall and Allen (5)) equations 24, 50, or 52 must be obeyed and one should not write separately:

$$\frac{(a_+^{(2)})^{\nu_+} (a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = 1, \qquad \frac{(a_+^{(3)})^{\nu_+} (a_-^{(3)})^{\nu_-}}{a_u^{(3)}} = K \tag{56}$$

IX. RÉSUMÉ. LIST OF THEOREMS

A certain number of the results obtained in the present paper may be considered as theorems. They are:

A. General theorems valid for all types of electrolytes and all concentrations

1. The activity coefficients of the solvent corresponding to the three descriptions of the solution (no dissociation, complete dissociation, incomplete dissociation) obey the relation:

$$\frac{f_1^{(1)}}{m + M} = \frac{f_1^{(2)}}{\nu m + M} = \frac{f_1^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

2. The osmotic coefficients obey the relation:

$$g_1^{(1)} \ln\left[1 + \frac{m}{M}\right] = g_1^{(2)} \ln\left[1 + \frac{\nu m}{M}\right] = g_1^{(3)} \ln\left[1 + \frac{[1 + (\nu - 1)\alpha] m}{M}\right]$$

3. The activity coefficient of the solute in the first description (no dissociation) and that of the undissociated solute in the third description (incomplete dissociation) are connected by the relation:

$$\frac{f_2^{(1)}}{m + M} = \frac{(1 - \alpha) f_u^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

4. The average activity coefficients of the ions in the second and third descriptions are connected by the relation (see equations 19, 22, and 23):

$$\frac{f_\pm^{(2)}}{\nu m + M} = \alpha \frac{f_\pm^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

B. Theorems valid for very low concentrations

Theorem 1:

$$f_1^{(1)} = f_1^{(2)} = f_1^{(3)}$$

Theorem 2:

$$g_1^{(1)} = \nu g_1^{(2)} = [1 + (\nu - 1)\alpha]\, g_1^{(3)}$$

Theorem 3:

$$f_2^{(1)} = (1 - \alpha)\, f_u^{(3)}$$

Theorem 4:

$$f_\pm^{(2)} = \alpha\, f_\pm^{(3)}$$

C. Theorems valid for very weak electrolytes at very low concentrations

When α is very small and $f_\pm^{(3)}$ is practically equal to unity, the solution being apparently ideal, theorems 3 and 4 of the foregoing series become:

$$f_2^{(1)} = 1 - \alpha \qquad (1)$$

$$f_\pm^{(2)} = \alpha \qquad (2)$$

X. SUMMARY

Three thermodynamic descriptions of solutions of electrolytes corresponding respectively to an undissociated, a completely dissociated, and an incompletely dissociated solute have been studied. Between the three sets of activity and osmotic coefficients certain thermodynamic relations are shown to hold. These are obtained in general form, and some interesting simple formulas are deduced for the particular case of very low concentrations and that of very weak electrolytes.

In concluding we wish to express our gratitude to Dr. J. W. McBain and Dr. F. O. Koenig, of this laboratory, for their valuable suggestions and comments.

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THE ACTIVITY AND OSMOTIC COEFFICIENTS OF AQUEOUS SOLUTIONS OF ACETIC ACID AT THE FREEZING POINT

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The purpose of the present investigation is to calculate from the freezing point data of Hausrath (2) and of Jones and Bury (3, 4) the activity and osmotic coefficients of aqueous solutions of acetic acid. As a typical illustration of the foregoing theory we shall determine these coefficients in the three thermodynamic descriptions corresponding respectively to an undissociated, a completely dissociated, and an incompletely dissociated solute. (Descriptions No. 1, 2 and 3.) The notation is the same as that of the previous paper (5).

For an electrolyte of the type of acetic acid ($\nu_+ = \nu_- = 1, \nu = 2$) it can easily be deduced from the theorems of the preceding paper (5) that:

$$[f_\pm^{(2)}]^2 = f_2^{(1)} \cdot K \cdot \frac{(2m + M)^2}{m\,(m + M)} \tag{1}$$

$$[f_\pm^{(3)}]^2 = f_2^{(1)} \cdot K \cdot \frac{[(1 + \alpha)\,m + M]^2}{\alpha^2 m\,(m + M)} \tag{2}$$

$$f_u^{(3)} = f_2^{(1)} \cdot \frac{(1 + \alpha)\,m + M}{(1 - \alpha)\,(m + M)} \tag{3}$$

We shall restrict ourselves to concentrations such that m, $2m$, $(1 + \alpha)m$ are small compared to M. Neglecting these quantities whenever they should be added to M amounts to using the Lewis-Randall coefficients γ. Therefore we shall write our formulas in terms of these γ's.

Remembering that

$$KM = K' \tag{4}$$

equations 1, 2, 3 become, in terms of the γ's,

$$[\gamma_\pm^{(2)}]^2 = \gamma_2^{(1)} \cdot \frac{K'}{m} \tag{5}$$

$$[\gamma_\pm^{(3)}]^2 = \gamma_2^{(1)} \cdot \frac{K'}{\alpha^2 m} \tag{6}$$

$$\gamma_u^{(3)} = \gamma_2^{(1)} \cdot \frac{1}{1-\alpha} \tag{7}$$

From equations 5 and 6 we deduce:

$$\gamma_\pm^{(2)} = \alpha\gamma_\pm^{(3)} \tag{8}$$

Between the three osmotic coefficients we have the relation:

$$g_1^{(1)} = 2g_1^{(2)} = (1+\alpha)\, g_1^{(3)} \tag{9}$$

Calling θ the freezing point lowering and λ the molar freezing point lowering (for water $\lambda = 1.858$), we have:

$$g_1^{(1)} = \frac{\theta}{\lambda m} \tag{10}$$

The divergence function j_1 of Lewis and Randall is given by:

$$j_1 = 1 - g_1^{(1)} = 1 - \frac{\theta}{\lambda m} \tag{11}$$

The activity coefficient $\gamma_2^{(1)}$ at a certain molality m and the activity coefficient $\gamma_{2,0}^{(1)}$ at another molality m_0 are connected by the relation:

$$\ln \frac{\gamma_2^{(1)}}{\gamma_{2,0}^{(1)}} = j_{1,0} - j_1 - \int_{m_0}^{m} j_1 \cdot d \ln m \tag{12}$$

On figure 1 the values of $-j_1$, deduced from the experimental results of Hausrath (2) and of Jones and Bury (3), are plotted against $\log_{10} m$. It will be seen that within the limits of experimental error the variation of $-j_1$ in terms of $\log_{10} m$ is linear. We found that it can be represented by the equation:

$$j_1 = 0.0371 \log_{10} m + 0.01484 \tag{13}$$

Equation 12 thus becomes:

$$\log_{10} \frac{\gamma_2^{(1)}}{\gamma_{2,0}^{(1)}} = \frac{j_{1,0} - j_1}{2.303} - 0.01855\,[(\log_{10} m)^2 - (\log_{10} m_0)^2] - 0.01484\,[\log_{10} m - \log_{10} m_0] \tag{14}$$

Equations 5, 6, 7, and 14 form a system of four equations with six unknowns: $\gamma_2^{(1)}$, $\gamma_{2,0}^{(1)}$, $\gamma_\pm^{(2)}$, $\gamma_\pm^{(3)}$, $\gamma_u^{(3)}$, and α.

In order to determine all these quantities we shall assume that the Debye-Hückel theory applies to the dissociated part of the solute, and we shall determine $\gamma_{2,0}^{(1)}$ at a certain low concentration from a knowledge of the true dissociation constant of acetic acid. From the value of $\gamma_{2,0}^{(1)}$ we shall then calculate $\gamma_2^{(1)}$ by means of equation 14 at concentrations for which j_1 is known. This procedure will thus enable us to avoid the graphic extrapolation of the j_1 curve to infinite dilution, which is particularly uncertain in this case.

By means of careful measurements of the E. M. F. of cells without liquid junction of the type

$$H_2 \mid HAc(m_1),\ NaAc(m_2),\ NaCl(m_3),\ AgCl \mid Ag$$

Harned and Ehlers (1) were able to determine the true dissociation constant of acetic acid at various temperatures. At 0°C. they found:

$$K' = \frac{\alpha^2 m}{1-\alpha}\cdot\frac{[\gamma_{\pm}^{(3)}]^2}{\gamma_u^{(3)}} = 1.653 \times 10^{-5} \tag{15}$$

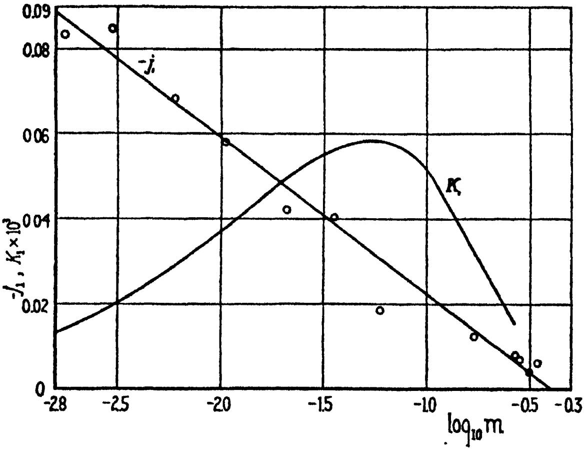

Fig. 1. j_1 and $K_1 = \frac{j_1^2 m}{1+j}$ for Aqueous Solutions of Acetic Acid

Freezing point measurements of Hausrath and of Jones and Bury

As shown by equation 9, $g_1^{(1)}$ and $1 + \alpha$ are practically identical at very low concentrations, since $g_1^{(3)}$ should then be very nearly equal to unity. We thus have approximately, at low concentrations,

$$-j_1 = \alpha \tag{16}$$

On figure 1 are plotted against $\log_{10} m$ the values of

$$K_1 = \frac{j_1^2\, m}{1 + j_1} \tag{17}$$

It will be seen that K_1 is by no means constant. At the concentration $m = 0.002138$ however, K_1 is exactly equal to K', i.e., 1.653×10^{-5}.

From equations 15, 16, and 17 we then deduce that at this particular concentration m_0 the following relation holds:

$$[\gamma_{\pm,0}^{(3)}]^2 = \gamma_{u,0}^{(3)} \tag{18}$$

For this concentration m_0 we have:

$$\alpha_0 = -j_{1,0} = 0.0843$$

The ionic strength $\alpha_0 m_0$ being very small we may assume, with a very high degree of approximation, that the mean activity coefficient of the ions obeys the Debye-Hückel limiting law, which in this case becomes:

$$\log_{10} \gamma_{\pm}^{(3)} = -0.5\sqrt{\alpha m} \tag{19}$$

TABLE 1

Activity and osmotic coefficients of aqueous solutions of acetic acid at 0°C.

m	$-j_1$	$g_1^{(1)}$	$g_1^{(2)}$	$g_1^{(3)}$	$\gamma_2^{(1)}$	$\gamma_{\pm}^{(2)}$	$\gamma_{\pm}^{(3)}$	$\gamma_{\mu}^{(3)}$	α
0.002138	0.0843	1.0843	0.5421	1.000	0.888	0.083	0.985	0.970	0.084
0.005	0.0705	1.0705	0.5352	1.008	1.122	0.061	0.980	1.199	0.062
0.01	0.0595	1.0595	0.5297	1.014	1.161	0.044	0.975	1.219	0.045
0.02	0.0485	1.0485	0.5242	1.016	1.192	0.031	0.971	1.232	0.032
0.05	0.0337	1.0337	0.5168	1.012	1.219	0.020	0.963	1.245	0.021
0.1	0.0225	1.0225	0.5112	1.007	1.229	0.014	0.956	1.248	0.015
0.2	0.0114	1.0114	0.5057	1.000	1.230	0.010	0.948	1.246	0.011
0.5	−0.0034	0.9966	0.4983	0.990	1.139	0.006	0.934	1.145	0.007

At the concentration m_0

$$\gamma_{\pm,0}^{(3)} = 0.9847$$

and, thanks to equation 18,

$$\gamma_{u,0}^{(3)} = 0.9696$$

The thermodynamic relation 7 gives then:

$$\gamma_{2,0}^{(1)} = (1 - \alpha)\, \gamma_{u,0}^{(3)} = 0.8879$$

and equation 14 becomes:

$$\log_{10} \gamma_2^{(1)} = 0.08362 - \frac{j_1}{2.303} - 0.01855\,(\log_{10} m)^2 - 0.01484 \log_{10} m \tag{20}$$

The values of j_1 corresponding to a certain number of round concentrations between m_0 and 0.5 are obtained from figure 1, and the corresponding coefficients $\gamma_2^{(1)}$ are then calculated by means of equation 20. From $\gamma_2^{(1)}$ we calculate $\gamma_{\pm}^{(2)}$ by means of equation 5. Knowing $\gamma_2^{(1)}$ we deduce α and $\gamma_{\pm}^{(3)}$ from the two simultaneous equations 8 and 19, which when combined give,

$$\frac{\gamma_{\pm}^{(2)}}{\alpha} = e^{-1.15\sqrt{\alpha m}} \tag{21}$$

or, at very low values of $\sqrt{\alpha m}$,

$$\frac{\gamma_{\pm}^{(2)}}{\alpha} = 1 - 1.15\sqrt{\alpha m} \tag{22}$$

$\gamma_{\pm}^{(2)}$ and m being known, we deduce from equation 22 a first and apparently sufficient approximation for α. $\gamma_{\pm}^{(3)}$ is then calculated by means of equation 19. $\gamma_2^{(1)}$ and α being known, $\gamma_u^{(3)}$ is calculated by means of equation 7. $g_1^{(1)}$ is known, $g_1^{(2)}$ and $g_1^{(3)}$ are calculated by means of equation 9.

All the numerical results are given in table 1. Those which are directly derived from the measurements ($-j_1$, $g_1^{(1)}$, $g^{(2)}$) are given to four decimal points. The others are given to only three decimal points.

As was to be expected, $\gamma_{\pm}^{(2)}$ is slightly smaller than α.

At infinite dilution we have:

$$\lim \gamma_{\pm}^{(3)} = 1 \tag{23}$$

From the theorems of our previous paper we then deduce:

$$\lim \gamma_{\pm}^{(2)} = 1 \tag{24}$$

We may assume that

$$\lim \gamma_{u}^{(3)} = 1 \tag{25}$$

We have shown that equation 24 leads to

$$\lim \gamma_{2}^{(1)} = 0 \tag{26}$$

An examination of table 1 will show that, somewhere at extremely low concentrations, $\gamma_{\pm}^{(2)}$ will increase rapidly so as to reach the value 1 at $m = 0$ and $\gamma_2^{(1)}$ will decrease to the value 0 at $m = 0$.

SUMMARY

The various activity and osmotic coefficients corresponding to the three thermodynamic descriptions (undissociated, completely dissociated, incompletely dissociated solute) for aqueous solutions of acetic acid are deduced from the best available freezing point data.

The value 1.653×10^{-5} of the dissociation constant at 0°C., determined by Harned and Ehlers, is used. The activity coefficients are obtained without the usual graphic extrapolation to infinite dilution, thanks to the combined use of the dissociation constant, of the Debye-Hückel limiting law, and of an empirical relation giving the dependence of the Lewis-Randall deviation function on molality.

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CATALYTIC DECOMPOSITION OF ACETALDEHYDE[1]

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I. INTRODUCTION

Acetaldehyde is a compound of very considerable activity. In gaseous form, under different conditions, it will undergo a number of different reactions of which the predominant one is the simple decomposition,

$$CH_3CHO \rightarrow CO + CH_4$$

A study of the equilibrium that results, with the possible reversal of the reaction to synthesize acetaldehyde from carbon monoxide and methane, is of interest from both theoretical and practical standpoints.

Thermodynamical calculations for this reaction have been made. Those based on generally accepted values (e.g., Parks and Huffman (5)) of free energies for the compounds involved indicate an equilibrium very unfavorable to synthesis. There is some uncertainty involved in such calculations, but to indicate a measurable partial pressure of acetaldehyde under the experimental conditions, the error in such free energy calculations would have to be at least 15,000 cals. It is true, however, that small amounts of acetaldehyde have been produced in the electric spark (3) and by the use of silent electric discharge (4). This paper gives the results of research on catalysts for this reaction.

II. CATALYSTS

Obviously the decomposition reaction is in this case most convenient for study of the catalysts; a dynamic method was first used. In order to test a material for catalytic activity some of it was placed in glass in a furnace, and activated by a stream of hydrogen. Then several grams of acetaldehyde were passed over the activated material by use of nitrogen as the inert carrier gas. Liquid products were removed by strong cooling, and were weighed and examined; fixed gases remaining were measured and then analyzed by the usual methods of absorption and combustion. Temperature, rate of flow of gases, volume changes, and presence of color, odor, and high-boiling fractions in the recovered liquids were also noted on each of the sixty-six runs.

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[1] From the thesis submitted to the Graduate School of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1932.

[2] Bill Raskob Foundation Fellow, 1929-33.

Metals for the catalysts were precipitated in the form of hydroxides, either pure or with supporting materials admixed. After being washed and dried, they were reduced in a stream of hydrogen at 300°C. for copper, 400°C. for nickel, and 500°C. for iron and cobalt, and cooled in an atmosphere of purified nitrogen.

Results indicate that copper is not a catalyst for this reaction. Other investigators (2) found that copper, on the contrary, favors condensation to form paraldehyde, metaldehyde, and crotonaldehyde. Iron shows very little activity, even at 300°C. Cobalt is more active than iron, but less so than nickel, which shows marked activity even below 200°C. Cobalt catalysts produce a relatively high hydrogen content in gaseous products, and are also sensitive to a slow poisoning effect, which Russel and Marschner (6) attribute to formation of crotonaldehyde.

Supported catalysts resemble the corresponding pure metals, but siliceous supporting materials also favor extensive side reactions, producing high-boiling liquids and a very low $CO:CH_4$ ratio. Catalysts made from amalgams were less active than the corresponding reduced metal, probably because of remaining traces of mercury, exceedingly difficult to remove.

A dark green, gel-like precipitate, formed by action of excess sodium hydroxide on an 8 per cent nickel nitrate solution was, after reduction, the material showing greatest activity and most freedom from side reactions. This catalyst was used in all subsequent equilibrium studies.

III. EQUILIBRIUM STUDIES

Preliminary studies indicated that in a steel bomb the decomposition of acetaldehyde was quite slow, the reaction continuing for at least one hundred and fifty hours. It also became evident that the temperature must be limited to 175°C. or above to prevent formation of nickel carbonyl, and to 225°C. or below to prevent formation of carbon dioxide and carbon. The presence of much carbon dioxide was found to aid in preventing resin formation as well as in suppressing carbon deposition, therefore its use was adopted.

In the adopted procedure, 25 g. of acetaldehyde was sealed in one thin-walled glass tube; in a similar tube 15 g. of catalytic material was reduced with hydrogen at 400°C. for three hours and sealed. Both sealed tubes were placed in the 485-cc. steel bomb, the bomb then closed, evacuated, filled with carbon dioxide to a pressure of 735 lbs. per square inch, and finally the glass tubes were smashed. Small samples of the contents were blown off at about twelve-hour intervals for analysis by a method similar to that of Ripper (1). This method involved collection of the sample over mercury, absorption in strong sodium bisulfite solution, and determination of acetaldehyde by the use of strong iodine solution and dry sodium bicarbonate, and titration with standard iodine solution. The method is reported to be satisfactorily specific for acetaldehyde in the presence of only small amounts of higher aldehydes, and involves a possible experimental error in absorption and titration estimated to be equivalent to 0.03 "per cent by volume." Residual gases were analyzed by absorption and combustion for carbon dioxide, carbon monoxide, methane, ethane, hydrogen and unsaturated hydrocarbons.

Table 1 contains the results of one run made according to the above procedure. The temperature was first held at 200°C., then lowered and held at 175°C. The increase in aldehyde content following the lowering of the temperature seems to indicate attainment of equilibrium, although the actual amounts present are quite small. A corresponding slight decrease of both carbon monoxide and methane content also occurred. On opening the bomb a very slight amount of free carbon and several cubic centimeters of liquid but no resinous material was found.

TABLE 1

Change of aldehyde in bomb

TEMPERATURE	ELAPSED TIME	ALDEHYDE
degrees C.	*hours*	*per cent by volume*
200 ±2	12	1 85
	35	1 74
	60	1 01
	108	0 38
	117	0 36
	141	0 28
	167	0 25
	179	0 25
175 ±2	204	0 28
	494	0 34
	515	0 31

Previously in the course of catalyst studies, an approximately equimolar mixture of carbon monoxide and methane was passed over an active catalyst at 175°C. and atmospheric pressure and through a liquid air trap. After the liquefied methane had boiled away, a definite odor of acetaldehyde was observed, and the rinsings of the bulb gave a weak positive test to fuchsine reagent. The results, however, could not be repeated.

Three attempts at synthesis were made by sealing in a glass tube of about 15-cc. volume, approximately 5.0 g of activated catalyst, 0.01 mole of liquid methane, and 0.02 mole of carbon monoxide in the form of nickel carbonyl, then heating the tube under high external pressure in a bomb at 170–190°C. for about sixty hours. Neither acetaldehyde nor any resin which would be evidence of temporary existence of acetaldehyde could be detected.

IV. SUMMARY

Numerous catalysts for the decomposition of acetaldehyde into carbon monoxide and methane have been studied; nickel precipitated by sodium hydroxide and reduced with hydrogen at 400°C. proved to be the best. Equilibrium conditions have apparently been attained in one direction, but attempts to approach them in the direction of synthesis were not very successful.

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ADSORPTION AT CRYSTAL–SOLUTION INTERFACES. VII[1]

EFFECT OF STIRRING AND GROWTH RATES ON THE HABIT AND DYE ADSORPTION OF ALUM CRYSTALS. INFLUENCE OF ACID AND ALKALI MEDIA ON THE HABIT OF ALUM CRYSTALS

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The present study is an extension of previous work carried out in this laboratory on adsorption at crystal–solution interfaces (2, 3, 4, 5, 10). Part I is concerned primarily with the effect of stirring on the habit of alum crystals, grown both from pure solutions and from solutions containing small quantities of dye. Part II deals with the influence of acids and alkalies on the habit of alum crystals.

I. EFFECT OF STIRRING AND RATE OF GROWTH ON THE HABIT AND DYE ADSORPTION OF ALUM CRYSTALS

Observations were made of the habit of individual potassium alum crystals grown both from stirred and from unstirred solutions. Quantitative measurements of the change in the relative growth rates of the cube and octahedral faces caused by stirring and by the adsorption of diamine sky blue were made and expressed in terms of the growth ratio V_{100}/V_{111} where V_{100} and V_{111} represent the relative rate of growth (i.e., perpendicular displacements) of the cube and octahedral forces respectively. The measurements were made by photographing the growing crystal every hour over periods ranging from twenty-four to forty-eight hours, using the apparatus and method described in previous papers. The growth ratios so obtained are given in table 1.

The above work was carried out in a constant temperature room held at 30°C. in which the humidity was controlled by the presence of open jars of calcium chloride. Further studies were made at about 23°C. (room temperature) with no effort to control the humidity. Potassium alum solutions containing varying concentrations of diamine sky blue were allowed to evaporate both with and without stirring and the resulting crystals analyzed colorimetrically to determine the amount of dye adsorbed. The results are given in table 2.

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[1] Presented in part before the Division of Colloid Chemistry at the Eighty-sixth Meeting of the American Chemical Society held in Chicago, September, 1933.

Ammonium alum solutions containing varying concentrations of crystal violet were allowed to crystallize by cooling solutions saturated at 30°C. to room temperature (23°C.). The crystals were filtered off and the filtrate allowed to evaporate at room temperature until another crop of crystals was obtained. The results of the colorimetric analysis of these crystals are given in table 3, in which the column headed "hot solution" refers to solutions saturated at 30°C. and "cold solution" to those saturated at 23°C.

From the results given in table 1 it is evident that the effect of stirring on potassium alum crystals grown both from pure solutions and from solutions containing varying concentrations of diamine sky blue is to decrease the size of the cube faces, i.e., to increase the V_{100}/V_{111} ratio. Other workers have observed a similar decrease in the size of cube faces in the case of potassium alum grown from supersaturated (8), rapidly cooling, or rapidly evaporating solutions (1). A consideration of Valeton's theory (9) of crystal growth suggests a plausible explanation. Valeton assumes that the actual rate of growth of any crystal face depends on two factors: (1) the specific rate of growth of that face (i.e., perpendicular displacement) which is dependent only on its ionic character, and (2) the speed with which the ions can diffuse to the face. Since the specific growth rate of the cube face is very high (because the face is populated by ions of like charge),

TABLE 1

Growth ratios of potassium alum crystals

SUBSTANCE	V_{100}/V_{111}	
	Stirred	Unstirred
Pure potassium alum	1.75	1.61*
Potassium alum + 0.002 g. of diamine sky blue per 100 cc.	1.66	
Potassium alum + 0.004 g. of diamine sky blue per 100 cc.	0.75	0.38
Potassium alum + 0.006 g. of diamine sky blue per 100 cc.	0.79	0.29
Potassium alum + 0.008 g. of diamine sky blue per 100 cc.	0.45	0.00

* Keenen and France (4).

TABLE 2

Adsorption of diamine sky blue by potassium alum crystals

DIAMINE SKY BLUE PER 100 CC. OF SOLUTION	PER CENT OF DYE ADSORBED	
	Stirred	Unstirred
grams		
0.002	0.008	0.01
0.004	0.017	0.04
0.006	0.055	0.09
0.008	0.080	0.13

the actual growth rate is determined by the rate of diffusion to the face. Any condition (such as stirring or growth from supersaturated, rapidly cooling, or rapidly evaporating solutions) which increases the rate of diffusion will increase the actual growth rate of the cube face and hence the V_{100}/V_{111} ratio.

The relatively greater size of the cube faces on crystals grown from unstirred solutions containing dyes than from stirred solutions can undoubtedly be accounted for in part by the same explanation that holds for crystals grown from pure solution. A second factor, smaller dye adsorption from stirred solutions as is shown in table 2, also is involved. The dye is adsorbed on the cube faces only, so that obviously the less color is adsorbed, the less the inhibiting effect on the growth rate of the cube faces, and the larger the V_{100}/V_{111} ratio. This lesser adsorption of color from stirred solutions can be explained by the increased rate of diffusion of the alum ions; since these ions are available, they will deposit on the crystal in preference to the foreign dye particles.

TABLE 3

Adsorption of crystal violet by ammonium alum crystals

CRYSTAL VIOLET PER 100 CC. OF SOLUTION AT 23°C	PER CENT OF DYE ADSORBED	
	Hot solution	Cold solution
grams		
0 03	0 0035	0 025
0 03	0 0028	0 023
0 04	0 0540	0 076
0 04	0 0550	0 084

It has previously been stated that the rate at which ions can reach the cube faces of alum is increased when crystals are obtained by rapid cooling or evaporation as well as by stirring. It should follow, then, that less color should be adsorbed by crystals grown by cooling warm solutions than by those produced by slow evaporation at room temperature. The results given in table 3 show that this prediction is verified experimentally.

II. INFLUENCE OF ACIDS AND ALKALIES ON THE HABIT OF ALUM CRYSTALS

Numerous workers have reported that alum crystallizes as cubes from alkaline solution; other investigators have reported changes in the habit of alum crystals grown in solutions containing various acids. Saylor (7) states that the influence of acid and alkaline solutions "upon external crystal form has served as a key to the entire field of adsorption and has tied in with those examples where adsorption has actually been demonstrated. The new technique is absolutely general"; and, further, "Negative ions are adsorbed on the octahedron faces of the alkali halides and barium nitrate, on the cube faces of potassium alum, and on the pyramids of sodium nitrate. The other principal faces adsorb positive ions." He has used as one of his examples the formation of large cube faces on alum crystals presumably grown from alkaline solutions or from other solutions containing readily adsorbable anions.

The present study was made to determine the influence of acid and alkaline media on the crystal habit of potassium and ammonium alum. The solutions were made up by adding the proper amounts of the foreign materials to saturated alum solutions. Individual seed crystals mounted on copper or nichrome wires were suspended in the solutions and allowed to grow over periods ranging from a few days to several weeks. The concentrations are expressed as the number of grams or per cent of foreign material per 100 grams of saturated solution.

Up to 25 or 30 per cent concentrations of hydrochloric, nitric, acetic, sulfuric, and phosphoric acids the crystals showed the usual cuboöctahedral form; the 110 face which frequently occurred in pure or slightly acid solutions tended to disappear at higher concentrations. Above 25 or 30 per cent, clumps of tiny crystals or needle-like formations formed in the nitric and phosphoric acid solutions, while crystal growth almost completely ceased in the other acids.

Crystals of potassium alum grown in 1 per cent sodium carbonate solution were similar to those grown from pure solution. When a 2 per cent sodium carbonate solution was used, some aluminum hydroxide precipitated; when this was filtered off and crystals allowed to grow in the clear filtrate, cubic crystals were formed and more aluminum hydroxide precipitated as the solution evaporated. Ammonium alum crystals in 1 per cent to 2 per cent sodium carbonate solutions were normal in habit. In 3 per cent solutions aluminum hydroxide was precipitated; crystals grown in the clear filtrate were cubic and more aluminum hydroxide precipitated as the solution evaporated.

The above results indicate that crystals grown from acid solutions do not show the enlargement of the octahedral faces predicted by Saylor's "absolutely general technique." Crystals grown in sodium carbonate solutions from which no aluminum hydroxide had precipitated showed no change in form; the cubic crystals obtained in solutions where some aluminum hydroxide had precipitated were not alum crystals but sodium or potassium sulfate.

III. SUMMARY

Stirring causes a decrease in the size of the cube faces of potassium alum crystals grown both from pure solution and from solutions containing varying concentrations of diamine sky blue. For a given concentration of dye, less color is adsorbed by crystals grown from stirred than from unstirred solutions, and by those obtained by rapid cooling than by slow evaporation at room temperature. An explanation is offered to account for these facts.

No appreciable change in habit occurs when alum crystals are grown from acid solutions or from solutions containing sodium carbonate from which no aluminum hydroxide has been precipitated.

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INFLUENCE OF THE PRESENCE OF A SOLUTE ON RATE OF OSMOSIS

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Most studies of osmotic phenomena have dealt with measurements of pressure with little reference to rates of transfer of material across the membrane. Although it is generally recognized that the presence of dissolved material affects the osmotic pressure exerted by a liquid, the influence of a solute on the rate of passage of the solvent through a semipermeable membrane has not been given serious consideration. For such a study two miscible liquids should be separated by a membrane which is permeable to one liquid and not to the other. Various substances should be dissolved in one of the liquids and the rates of osmosis compared with those obtained using the pure solvents. In the work described below a system composed of pyridine-rubber-water was used.

If a water-soluble salt such as silver nitrate is dissolved in the pyridine, the flow through the rubber should be retarded, but not to the same extent as when a water-insoluble compound, such as anthracene, is dissolved in the pyridine. On the other hand an aqueous solution of potassium chloride, a salt which is insoluble in pyridine, should also retard the flow, because the aqueous solution has less attraction for the pyridine and thus should pull it through the rubber membrane less rapidly.

EXPERIMENTAL

The apparatus, materials, and method of experimentation were identical with those described in a paper (1) dealing with the effect of temperature on rate of osmosis. Since 35°C. was a convenient temperature at which to work and gave rates of flow large enough to be conveniently measured, the experiments were conducted at that temperature. It was pointed out in the previous paper that at 35°C. the determination of rates in the pyridine–rubber–water system could be duplicated with a high degree of accuracy.

Early in the investigation it was noticed that pyridine, after standing in contact with the same rubber membrane for some time, contained fine particles of dispersed material. Substituting this contaminated pyridine for the pure solvent showed that the suspended particles and dissolved material which were present exerted a definite retarding action on the passage of the liquid through the membrane. It was this discovery that prompted the use of freshly distilled pyridine and a new rubber membrane in each determination.

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[1] Present address, 116 Elm Ave., Rahway, New Jersey.

[2] Present address, 912 Haskell Ave., Rockford, Illinois.

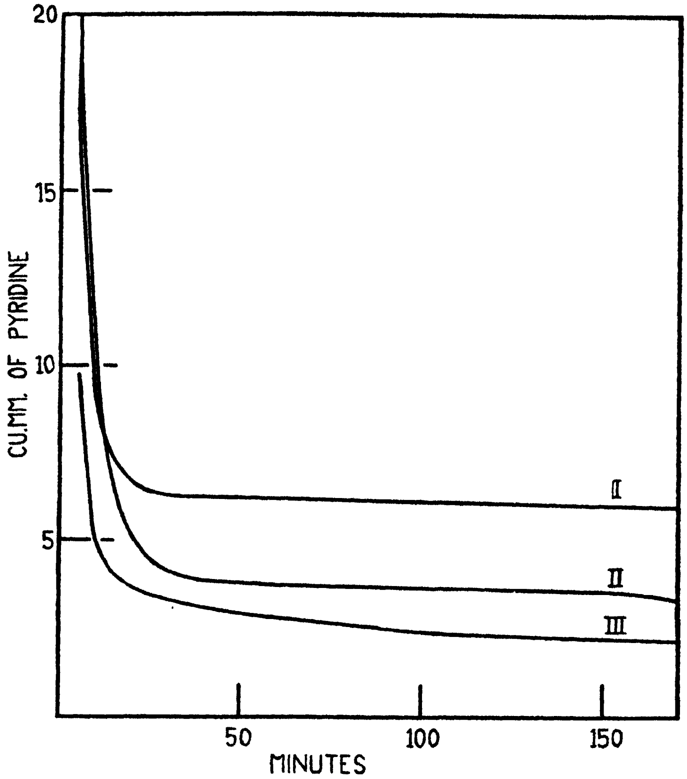

FIG. 1. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING SILVER NITRATE IN THE PYRIDINE

Curve I, pyridine–water; curve II, 0.5 *N* silver nitrate in pyridine–water; curve III, 1.0 *N* silver nitrate in pyridine–water.

The data obtained are given in figures 1 to 4 inclusive.

DISCUSSION

The rates of osmosis are found to be very regular except at the beginning of the experiments. Irregularities may occur at the start of each experiment because a few minutes must elapse before the membrane becomes saturated with pyridine and a steady rate of flow is attained. For this

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ERRATUM

Vol. 39, pp. 432–5: The ordinates of figures 1 to 4 should be labelled "of pyridine per square centimeter of membrane."

reason no deductions should be made until about thirty minutes after the beginning of the experiment, when the rates become constant. From thirty minutes on up to seven to ten hours the rates of osmosis at 25°C. to 35°C. are very uniform for every combination studied.

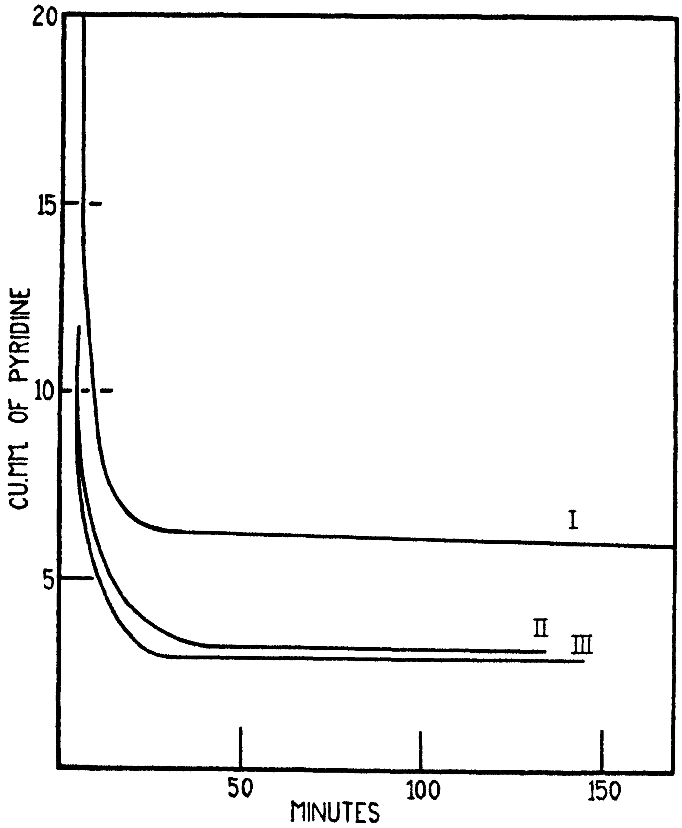

FIG. 2. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING ANTHRACENE IN THE PYRIDINE

Curve I, pyridine-water; curve II, 0.08 *M* anthracene in pyridine-water; curve III, 0.16 *M* anthracene in pyridine-water.

Organic and inorganic solvents in either of the liquids retard the dialysis rate. It might be expected that a molar solution of silver nitrate in pyridine would hold back the pyridine twice as much as a half molar solution, but this is not found to be true (figure 1). Successive equal amounts of added solute make increasingly smaller changes in the rate of passage. Doubling the amount of anthracene in the pyridine (figure 2) has a smaller relative effect than doubling the concentration of silver nitrate. Considering the effects of equal molar quantities of anthracene and silver nitrate, the organic compound is more effective than the silver salt in retarding the passage of the pyridine through the rubber membrane.

Figure 3 shows that an aqueous molar solution of sucrose draws pyridine through a rubber membrane more slowly than a molar solution of potassium chloride. However, with both solutions the rate of passage is slower than with pure water.

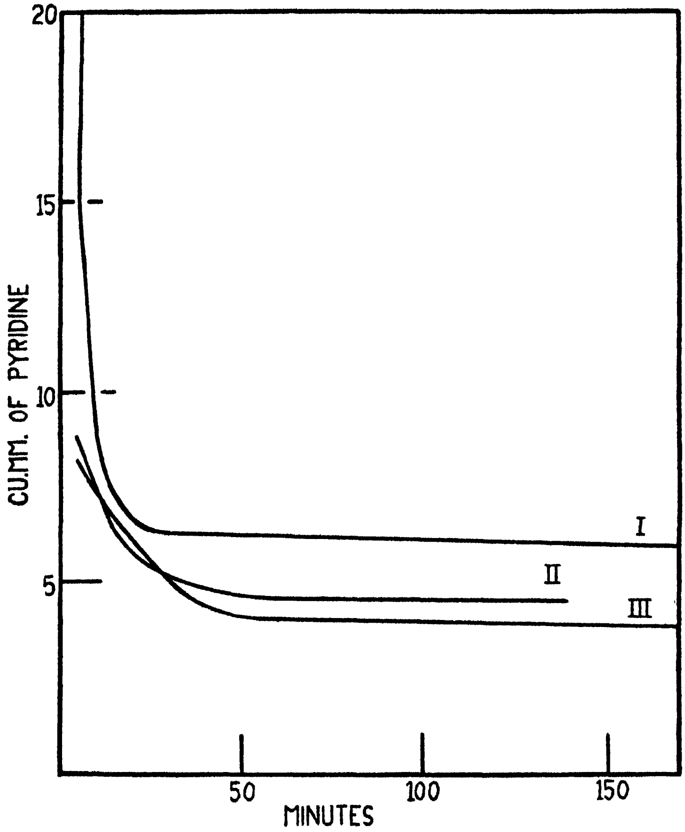

FIG. 3. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING POTASSIUM CHLORIDE AND SUCROSE IN THE WATER

Curve I, pyridine–water; curve II, pyridine–molar solution of potassium chloride in water; curve III, pyridine–molar solution of sucrose in water.

As mentioned above, when pyridine is allowed to stand in contact with rubber for many hours the liquid becomes contaminated with dissolved and dispersed material derived from the membrane. If such contaminated pyridine is used in a new experiment with a fresh rubber membrane the rate of passage of the pyridine into the water is found to be greatly retarded (figure 4).

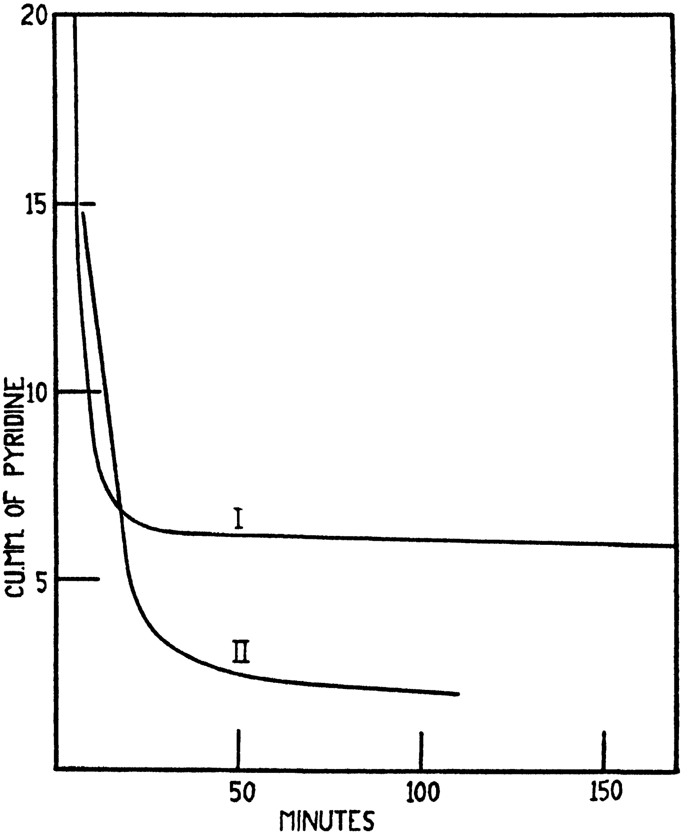

FIG. 4. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY THE PRESENCE OF FOREIGN PARTICLES IN THE PYRIDINE

Curve I, pyridine-water; curve II, foreign particles in pyridine-water

SUMMARY

1. The retardation of the rate of osmosis of pyridine through a rubber membrane into water, which is caused by dissolving silver nitrate and anthracene in the pyridine, was determined at 35°C.

2. The effect of dissolving sucrose and potassium chloride in the water was determined for a pyridine-rubber-water system at 35°C.

3. The influence of dissolved and dispersed rubber in the pyridine on the rate of osmosis was determined.

REFERENCE

(1) TRAXLER, R. N.: J. Phys. Chem. **32**, 127-41 (1928).

NEW BOOKS

Volumetric Analysis. By H. P. STARCK. 228 pp. Baltimore: William Wood & Company, 1934. Price: bound, $3.00.

This book is written primarily for pharmaceutical and medical students and seems to be suitable for the purpose. However, it cannot be recommended as a text for students in chemistry, since the theory is entirely inadequate, a great many of the procedures are repetitions and not up-to-date, and some of them are highly inaccurate.

I. M. KOLTHOFF.

Dipole Moments. A General Discussion held by the Faraday Society. 25 x 16 cm.; lxxxvi + 227 pp. London: Gurney and Jackson, 1934. Price: (in stiff cloth covers) 21s.

This volume, reprinted from the Transactions of the Faraday Society, contains twenty-four papers and a general discussion on dipole moments and related topics, which were communicated at the Faraday Society's Symposium at Oxford in April, 1934.

The papers, which include contributions from the leading workers in this field in America and Europe, are divided into three groups: Part I. Dielectric Constant; Part II. Determination of Dipole Moments; Part III. Interpretation of Dipole Moments.

The first section begins, as is fitting, with a paper by Debye, on "Energy Absorption in Dielectrics with Polar Molecules." The other two papers in this section deal with the temperature variation of the dielectric constant of some crystalline solids.

The nine papers in the second section are mainly concerned with the dielectric behavior of concentrated solutions, dipole association, and cohesion, and with the difficulties encountered in the calculation of dipole moments from polarization measurements in solution, in particular, the vexed question of the atom polarization, and the effect of the non-polar solvent on the apparent dipole moment. These papers constitute a valuable summary of the present position in these matters.

The third section contains papers which cover a very wide field of the application of dipole moment measurements to problems of molecular and stereochemical structure.

An appendix of some eighty-six pages contains an excellently arranged catalogue of dipole moment data compiled by Dr. N. V. Sidgwick and his collaborators. This is the most complete list of dipole moments which has been published, and would in itself render the volume invaluable as a book of reference. In this list are given, not only the actual dipole moments, the authors, and references, but also the temperature or temperature range of measurement, the solvent or medium in which the measurement was carried out, the method used for the elimination of P_e, the allowance which has been made for P_a, and the observed value of $_\infty P_2$ where this is given by the author.

The book is indispensable to workers in the field of dipole moments and contains much of interest to the general reader.

F. FAIRBROTHER.

Leitfähigkeitstitrationen und Leitfähigkeitsmessungen. Visuelle und akustische Methoden. By G. JANDER and O. PFUNDT. 25 x 16 cm.; viii + 88 pp. Stuttgart: F. Enke Verlag, 1934. Price: unbound, 7.40 RM; bound, 8.80 RM.

This book constitutes the second edition of Prof. Jander's excellent monograph on visual conductometric titrations. Since its appearance, he and his pupils have made several improvements in the technique of these methods, and these are described in the present volume. As its name implies, the new edition has been extended so as to cover the whole field of conductometric analysis, including its technical applications. Coming, as it does, from the pens of well-known authorities in the field of physico-chemical analysis, the volume will be heartily welcomed by physical chemists, analysts, and especially those engaged in many chemical industries.

The introduction of satisfactory and accurate visual methods has undoubtedly rendered conductometric methods available in noisy works laboratories, in which the ordinary telephone method cannot be used, and it is there that Jander's technique will find ever-increasing adoption.

The second half of the book deals with analytical processes. Although, from the purely practical standpoint, the descriptions are adequate, it is felt that too little attention is given to the principles underlying the procedures, and this is especially the case in the section on acidimetry and alkalimetry, in which no attempt is made to correlate the shape of the titration graphs with the dissociation constants of acids and bases and the concentrations of the solutions being titrated and their titrants. On titrations themselves, the book can hardly be regarded as exhaustive.

H. T. S. BRITTON.

The Electronic Structure and Properties of Matter. By C. H. DOUGLAS CLARK. 22 x 14 cm.; xxv + 374 pp. London: Chapman and Hall, Ltd., 1934. Price: 21s.

This book is the first volume of a Comprehensive Treatise on Atomic and Molecular Structure, of which two further volumes, treating of the fine structure of matter and the interpretation of band spectra, respectively, are in preparation. This volume consists of two parts, a general introduction and a treatment of physical properties and molecular constitution.

The general introduction gives a survey of modern views on the Periodic Table, the electronic configuration of atoms, quantum numbers, the transition elements, valency, and the nature of chemical linkages. The treatment is brief, accurate, and reasonably clear, though too condensed to be of much value to the student approaching the subject of electronic structure for the first time. It is a pity that Dr. Clark has not given a fuller and clearer treatment to this portion, and so made it a very valuable textbook for the university student.

The second portion collects a great number of facts which have not been assembled before in a single volume. This section will certainly be of great value. It contains excellent surveys of melting and boiling points, atomic and molecular volumes, atomic and ionic radii, electrical conductivity, magnetic and cohesional properties. The reviewer, though naturally unable to test the accuracy of the whole of a work of this type, has found no errors other than minor misprints.

Full references are given to the author's sources, and their clear and detailed presentation is a valuable feature of the work. The indexes are not so complete. A short examination revealed the absence of the names of Wasastjerna and Kerschbaum from the author index and of permutites (pp. 150, 151), rectification (p. 190), and complex compounds (pp. 225–8) from the subject index.

FRANK SHERWOOD TAYLOR.

THE ELECTROCAPILLARY CURVE AND ITS DISPLACEMENT WITH CONCENTRATION AND TEMPERATURE[1]

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Received June 14, 1934

INTRODUCTION

A change in the electrical potential across the interface formed by an aqueous solution in contact with mercury is accompanied by a change in interfacial tension which can be measured directly. The relationship between interfacial tension and applied potential may be represented graphically, forming the so-called electrocapillary curve. If we plot some function of interfacial tension as ordinate with applied potential as abscissa a curve of parabolic shape is usually obtained.

Before a difference of potential is applied across the interface the mercury is positively charged and anions are preferentially adsorbed in the solution side of the interface. Usually the anions are capillary-active. In this event the more capillary-active the anion is, the greater will be the depression in the rising branch of the curve. As the applied potential difference is increased the charge of the mercury surface is lowered, thus increasing the interfacial tension and causing the electrocapillary curve to rise. A maximum in the curve is reached when the charge on the mercury surface has been neutralized. Further increase in applied potential causes the mercury to become negatively charged, and the curve descends. If the cations are capillary-active, the descending branch of the curve will be depressed because of the increased concentration of these ions at the interface. The general mathematical theories of the electrocapillary curve have been presented and discussed in a number of places in the literature. Reference may be made at this time to articles by Lippmann (11), Gouy (5), Frumkin (3), Koenig (8), and Craxford, Gatty, and Philpot (1).

The electrochemical study of the interfacial potential difference between mercury and a solution containing electrolytes, or electrolytes and neutral molecules, is important because a knowledge of the effects produced gives information about the properties and arrangement of the ions and molecules present in the interface. In this report it will be our purpose to give the results of a study of the effect of changes in temperature and concentration of ammonium nitrate in aqueous solution on the position and shape of the electrocapillary curve.

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[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

More complete details of this work may be found in the thesis of L. A. Hansen, presented to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy and filed in the Library of the University of Wisconsin, June, 1934.

In a later report there will be presented the results of similar electrocapillary studies with solutions of sodium sulfate and of certain nonelectrolytes.

PREPARATION OF MATERIALS

Mallinckrodt's "Reagent Quality" sodium sulfate was used. Mallinckrodt's "C.P." quality ammonium nitrate was recrystallized from water and dried in a desiccator over concentrated sulfuric acid for use. The mercury was purified by placing concentrated sulfuric acid over it and passing air through the liquids. This process was continued for a period of a week, the sulfuric acid being changed several times. After this treatment the mercury was thoroughly washed to remove all traces of acid; then it was dried and distilled. Mercurous nitrate was prepared by allowing concentrated nitric acid to react with an excess of the purified mercury. The mercurous nitrate was removed from the solution by filtration through a sintered glass filter and was dried over concentrated sulfuric acid in a desiccator.

All of the solutions were prepared by dissolving the proper weights of the materials in conductance water. The final distillation of the conductance water was carried out in quartz.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus employed in this research was constructed of Pyrex glass. It is shown diagrammatically in figure 1. The liquid to be studied was placed in the cell T, which was connected to the electrometer proper by means of the ground glass joint S. The side arm U was joined with K, a reflux condenser. Because of the fact that temperatures of from 25° to 75°C. were to be used, it was necessary to employ this reflux condenser to keep the pressure in the cell equal to the atmospheric pressure without changing the composition of the solution.

The column of mercury P ends in the capillary L. The inside radius of the capillary was approximately 6×10^{-4} centimeter. Because the capillary was so small, the technique ordinarily used in sealing capillary tubing to larger tubing could not be employed. Eight-millimeter Pyrex tubing was used, because the outside diameter of the capillary tubing was just slightly less than the inside diameter of tubing of this size. The capillary tube was inserted to a distance of about one-fourth of an inch into the 8-

mm. tubing. The two tubes were then clamped in this position on a ring stand. The glass tubing which extended over the capillary tubing was heated gently with a hand blast torch until a small portion of it became soft. This pliable portion was pressed against the capillary tubing by rolling a carbon rod over the surface. This process was continued until the capillary tubing was entirely sealed into position. By following this method it was possible to seal capillary tubes without collapsing their inner walls. The stopcock J and the ground glass joint R made it possible to take the apparatus apart whenever it was necessary to replace the capillary tip L. Two brass rings were clamped on the tube; one above, and one below, the joint R. Metal springs were suspended between the two brass rings, thus holding the ground glass joints securely in position. The height of the mercury in column P could be changed by applying pressure from a nitrogen tank through the tube F.

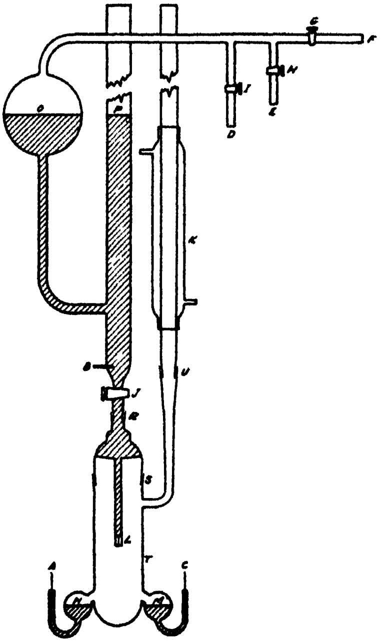

FIG. 1. APPARATUS

The negative electrode, located at B, consisted of a tungsten wire sealed into the glass tube. The tungsten wires A and C were sealed into the glass vessel coming in contact with the duplicate anodes of mercury, N and M respectively.

The stopcock H allowed the pressure in the reservoir O to be reduced by allowing nitrogen gas to escape to the atmosphere through it. When the stopcock I was opened, the pressure was moderated by having another reservoir connected to the outlet D.

The entire electrometer was placed in a well-insulated air thermostat. The heating elements consisted of nichrome wire wound in spiral form. The air was thoroughly circulated by means of a fan, the blades of which were placed inside the air bath, while the motor which drove the fan was located outside the thermostat. The temperature was regulated by means of relay and deKhotinsky regulator.

The difference of potential to be applied across the electrodes A and B was obtained by means of an ordinary potentiometric circuit.

The mercury in the capillary tip L was illuminated by means of an automobile spotlight and a lens which focused the light on the capillary. The source of light was placed at right angles to the telescope of the comparator. It was found that by having the distance from the objective of the comparator to the mercury capillary very slightly greater than the focal length of the telescope, the mercury in the capillary took on the appearance of a wide ribbon with well-defined tip. If the comparator was so arranged that it was sharply in focus, it was observed that the mercury in the capillary would take on the appearance of a fine thread with a diffuse or ill-defined tip. Instead of measuring the change of position of the mercury in the capillary, it was more convenient to keep the mercury at a constant level by increasing or decreasing the height of the mercury in the column P.

The position of the mercury in the capillary L was kept constantly at a point 0.05 cm. from the lower tip of the capillary. It was found by Koenig (9) that if the mercury was kept at a position such that it was more than 0.1 cm. from the end of the capillary the slight amount of hydrogen which was slowly liberated at the capillary cathode could not diffuse out fast enough but would form bubbles of hydrogen inside.

The height of the mercury in column P was measured by means of a traveling telescope suspended on a $\frac{3}{4}$-in. cold rolled steel rod and a steel scale graduated to millimeters. The distance from the mercury meniscus in the capillary to the bottom of the steel scale was a constant for each capillary, so the height actually measured with the traveling telescope is the difference between the bottom of the scale and position of the mercury meniscus in the tube P. The distance from the mercury meniscus in the capillary to the bottom of the steel scale was measured by means of a cathetometer.

The solution in the cell T extended a short distance above the bottom of the capillary tip L. In order to make the correction for the hydrostatic pressure of this column of solution from the bottom of the mercury meniscus to the top of the solution it was necessary to measure this height accurately. This measurement was made by means of the comparator.

To obtain the values of the interfacial tension in absolute units from the corresponding heights of the mercury column the following procedure was adopted. The value of the interfacial tension at the maximum of the electrocapillary curve for a half-molar aqueous solution of sodium sulfate has been determined by Gouy (6). The apparatus was calibrated by means of this solution for each capillary used.

EXPERIMENTAL RESULTS

Electrocapillary curves were obtained at 25°, 50°, and 75°C. for the following solutions of ammonium nitrate: (1) 1.0 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid. (2) 0.2 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid. (3) 0.02 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid.

The electrocapillary data are collected to form table 1. In the first column are found the values of ϕ, the applied potential difference. The second, third, and fourth columns contain values of interfacial tension corresponding to the several applied potential differences at 25°, 50°, and 75°C., respectively, for 1.0 *M* ammonium nitrate solution; the fifth, sixth, and seventh columns are made up of similar data for the 0.2 *M* solution; and the eighth, ninth, and tenth columns contain the results for the 0.02 *M* solution. Representative electrocapillary curves which show the effect of change in concentration and temperature, plotted from these data, are shown in figures 2 and 3.

In order to determine accurately the position of the maximum of an electrocapillary curve, an equation for a portion of the curve extending to a short distance on either side of the apparent maximum was obtained by the method of the least squares. The first derivative $\frac{d\sigma}{d\phi}$, when equated to zero, gave the exact position of the curve. This method of obtaining the maximum was used in all cases. In table 2 there are given representative results obtained at 25°C. The heading for each column is self-explanatory. Such results are shown graphically in figure 4. The curves of this figure are from values obtained by using the mathematical equations, but the points on the curves are experimental values.

The results of calculations for ϕ (max.) and for the coefficients $\frac{\partial\sigma\ (\text{max.})}{\partial T}$ and $\frac{\partial\phi\ (\text{max.})}{\partial T}$ for the ammonium nitrate solutions are summarized in table 3. In the third column are given the values of the applied potential which correspond to the maxima of the electrocapillary curves. The fourth column presents the differential coefficient of change of σ (max.) with temperature, and the last column gives the corresponding coefficient for change of ϕ (max.) with temperature.

TABLE 1

Electrocapillary data for ammonium nitrate solutions

ϕ	1.0 *M* NH_4NO_3 25°C.	1.0 *M* NH_4NO_3 50°C.	1.0 *M* NH_4NO_3 75°C.	0.2 *M* NH_4NO_3 25°C.	0.2 *M* NH_4NO_3 50°C.	0.2 *M* NH_4NO_3 75°C.	0.02 *M* NH_4NO_3 25°C.	0.02 *M* NH_4NO_3 50°C.	0.02 *M* NH_4NO_3 75°C.
volts	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$
0.000	312.57	314.78	315.61	306.27	306.99	307.74	310.46	311.32	310.64
0.025	319.26	321.52	322.20	312.73	313.93	313.98	317.03	317.59	316.97
0.050	325.41	327.72	328.17	319.18	319.93	320.22	322.67	323.98	322.59
0.075	331.43	333.21	333.80	325.37	325.92	326.08	329.12	329.39	328.41
0.100	337.11	338.82	339.11	331.47	331.77	331.86	334.72	334.89	333.80
0.125	342.47	343.96	344.31	337.34	337.22	337.02	339.73	340.07	339.07
0.150	347.48	348.99	349.12	342.27	342.52	342.10	344.82	345.13	344.19
0.175	352.33	353.62	353.89	347.13	347.39	347.18	350.41	349.92	349.15
0.200	356.95	358.22	358.42	351.94	352.22	351.95	355.30	354.56	353.96
0.250	365.75	366.52	366.64	361.41	360.99	360.67	363.95	363.29	361.91
0.300	373.85	374.43	374.17	369.90	369.32	368.47	372.29	371.47	369.79
0.350	380.94	381.64	381.07	377.57	376.96	375.84	379.88	378.83	376.81
0.400	387.71	388.10	387.32	384.77	383.89	382.70	386.96	385.88	383.36
0.450	393.85	393.91	392.94	391.19	390.32	388.48	393.38	392.04	389.68
0.500	399.45	399.28	397.98	397.45	396.17	394.41	399.33	397.72	394.84
0.550	404.34	403.88	402.44	403.08	401.43	399.30	404.54	402.44	399.53
0.600	408.65	407.74	405.93	407 82	405.94	403.60	409.31	406 92	403.64
0.650	412.48	411.48	409.23	412.48	410.62	407.17	413 65	410.85	406.90
0.675	414.16	412.68	410.27	414.63	412.22	409.03	415.57	412.41	408.49
0.700	415.65	414.40	411.40	416.24	413.85	410.58	417 65	413.93	409.77
0.725	416.82	415.37	412.37	417.80	415.45	411.71	419.17	415 33	411.01
0.750	418.00	416.35	413.11	419.25	416.81	412.68	420.78	416 50	411.98
0.775	419 05	417.24	413.53	420.54	417.75	413.49	421 99	417 63	412.91
0.800	420.07	417 71	414.08	421.72	418 53	414 42	422.85	418.45	414.00
0.825	420.66	417.98	414.39	422.81	419.35	414.93	423.44	419.15	414.58
0.850	421.09	418.10	414.42	423.59	420.01	415.39	424 30	419.81	415.39
0.875	421.21	418.10	414 27	424.06	420 36	415.63	424 69	420.36	415.98
0.900	421.21	418.02	413 80	424 30	420.52	415.78	425.04	420.79	416.40
0.925	421.05	417.75	413.34	424.49	420.59	415.78	425.39	421.18	416 52
0.950	420.62	417 36	412.72	424.49	420.52	415.70	425.47	421.37	416.52
0.975	419.92	416.39	411.90	424.34	420.36	415.55	425 47	421.22	416.44
1 000	419 09	415.37	410.78	424.02	419.97	415.00	425.36	421 06	416.25
1.025	418.15	414.52	409 62	423 28	419.11	414.23	425 28	420.79	413.05
1.050	417.14	413.23	408.53	422.41	418.06	413.45	424.85	420.40	415.70
1.075	416.16	411.59	407.13	421.17	416.58	412.49	423.91	419.62	415.04
1.100	414.40	410.31	405.58	419.99	415.65	411.44	423.05	418.84	414.35
1.125	412.68	408.40	404.22	418.70	414.13	410.35	422.07	418.02	413.53
1.150	410.91	406.53	402.56	417.18	412 68	408.88	421 17	416.89	412.37
1.175	408.92	404.66	400.77	415.65	411.17	407.64	419.88	415.61	411.13
1.200	406.88	402.91	398.91	414.08	409.30	405.85	418.43	414.28	409.93
1.225	404.65	401.23	396.82	412.32	407.66	404.65	416.94	413.00	408.80
1.250	402.27	398.62	394.57	410.33	406.06	402.79	415.38	411.67	407.68
1.275	399.76	396.13	392.32	408.25	404.31	401.01	413.42	410.23	406.47
1.300	397.37	393.56	389.68	406.26	401.78	399.18	411.58	408.36	404.88
1.350	391.93	388 88	384.33	401.52	397.69	394.76	408.14	404.39	401.94
1.400	385.87	382.65	378.63	396.55	392.70	389.95	403.67	400.69	397.44
1.450	379.45	376.49	372.97	391.58	387.75	385.03	399.17	396.05	392.86
1.500	372 52	369 71	365.99	385.13	382.22	379.13	393.62	390.99	388.21
1.550	365.52	362.78	359.20	378.59	375.95	373.20	388.02	385.65	383.48
1.600	357.81	355 03	351.83	371.86	369.21	367.11	381.68	383.74	377.58

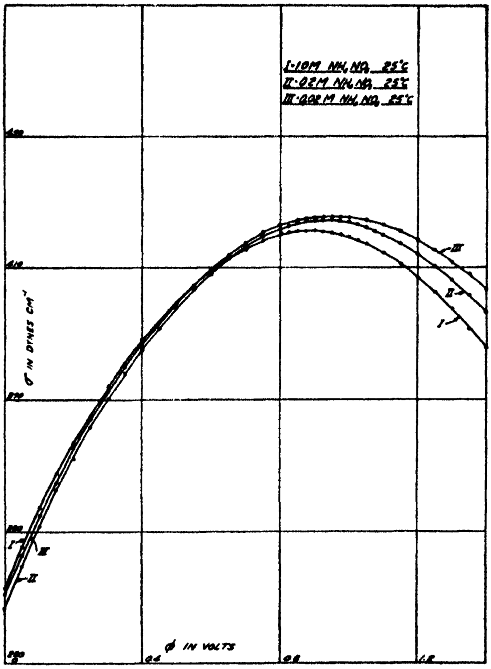

FIG. 2. ELECTROCAPILLARY CURVES FOR 1.0 M, 0.2 M, AND 0.2 M AMMONIUM NITRATE SOLUTIONS AT 25°C.

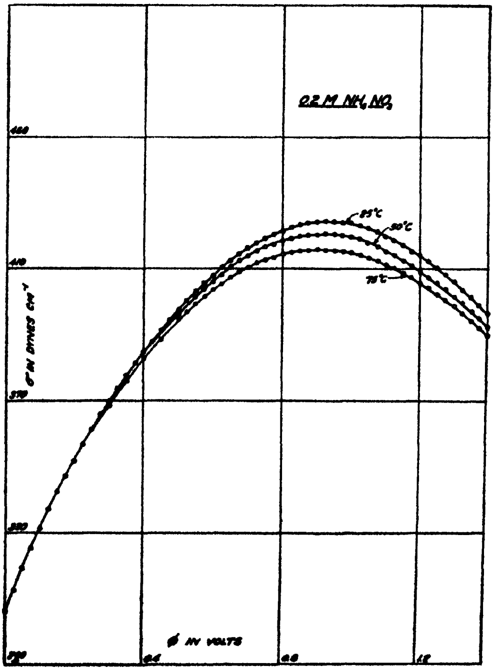

FIG. 3. ELECTROCAPILLARY CURVES FOR 0.2 M AMMONIUM NITRATE SOLUTION AT 25°, 50°, AND 75°C.

TABLE 2

Data for 0.2 M ammonium nitrate solution at 25°C.

ϕ	σ OBSERVED	σ CALCULATED	DEVIATION	DEVIATION SQUARED
volts	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$		
0.825	422.81	422.81	0.00	0.0000
0.850	423.59	423.52	−0.07	0.0049
0.875	424.06	424.06	0.00	0.0000
0.900	424.30	424.39	+0.09	0.0081
0.925	424.49	424.54	+0.05	0.0025
0.950	424.49	424.51	+0.02	0.0004
0.975	424.34	424.29	−0.05	0.0025
1.000	424 02	423.88	−0.14	0.0196
1 025	423.28	423.28	0.00	0.0000
1.050	422.41	422.48	+0.07	0.0049
			−0.03	0.0429

σ (max.) = 424.49 dynes cm.$^{-1}$ ϕ (max.) = 0.933 volt

$$\sigma = 293.52 + 280.96\phi - 150.60\phi^2$$

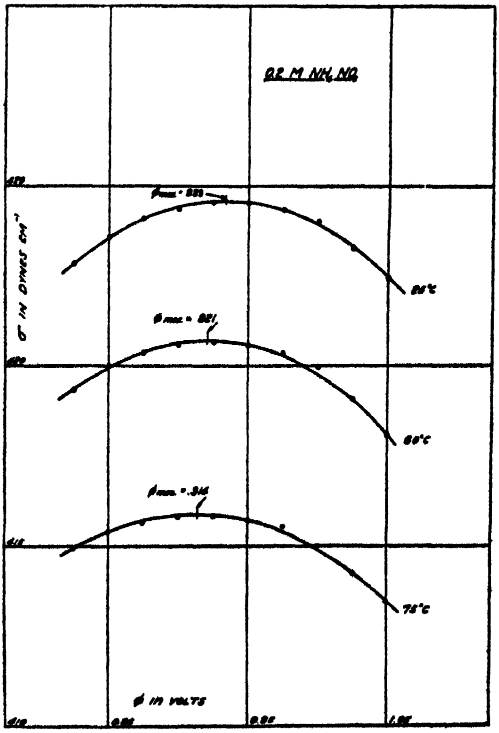

FIG. 4. ELECTROCAPILLARY CURVES FOR 0.2 *M* AMMONIUM NITRATE SOLUTION IN THE REGION OF THE MAXIMA OF THE CURVES AT 25°, 50°, AND 75°C.

In measurements carried out at 27.5°C., the potential of the 1.0 *M* ammonium nitrate solution in contact with mercury with respect to the normal calomel electrode was found to be 0.338 volt, that of the 0.2 *M* solution 0.385 volt, and that of the 0.02 *M* solution 0.414 volt.

TABLE 3

Summary of electrocapillary data

SOLUTION	TEMPERATURE	ϕ(max.)	$\frac{\partial\sigma(\text{max.})}{\partial T}$	$\frac{\partial\phi(\text{max.})}{\partial T}$
	°*C.*	*volts*	*dynes cm.$^{-1}$ degree^{-1}*	*volts degree^{-1}*
1.0 *M* NH_4NO_3	25	0.887		
1.0 *M* NH_4NO_3	50	0.862	−0.12	−0.00100
1.0 *M* NH_4NO_3	75	0.846	−0.15	−0.00064
0.2 *M* NH_4NO_3	25	0.933		
0.2 *M* NH_4NO_3	50	0.921	−0.16	−0.00048
0.2 *M* NH_4NO_3	75	0.914	−0.19	−0.00028
0.02 *M* NH_4NO_3	25	0.961		
0.02 *M* NH_4NO_3	50	0.961	−0.16	−0.0000
0.02 *M* NH_4NO_3	75	0.953	−0.19	−0.00032

TABLE 4

Electrical capacity data for 0.2 M ammonium nitrate solution at constant potential values

ϕ	$\frac{d\sigma}{d\phi}$ IN COULOMBS CM.$^{-2}$ × 10^7		
	At 25°C.	At 50°C.	At 75°C.
0.825	32.47	28.61	22.71
0.850	24.94	21.21	16.34
0.875	17.41	13.74	9.97
0.900	9.88	6.27	3.60
0.925	2.35	−1.20	−2.77
0.950	−5.18	−8.67	−9.13
0.975	−12.71	−16.14	−15.50
1.000	−20.24	−23.61	−21.87
1.025	−27.77	−31.08	−28.24
1.050	−35.30	−38.55	−34.61

The Lippmann equation for the electrocapillary curve is $\frac{d\sigma}{d\phi} = \epsilon$, where ϵ is the electrical capacity of the surface at constant potential. The value of ϵ can be calculated from the slope of the electrocapillary curve. If the equations for these curves, $\sigma = a + b\phi - c\phi^2$, are differentiated with respect to ϕ, values of ϵ are obtained. Data of this sort are presented in table 4.

DISCUSSION

For discussion it is convenient to divide the electrocapillary curves into three parts, an ascending branch, a maximum, and a descending branch.

The ascending branch

Along the ascending branch the mercury is positively charged and, as a result, there is an excess of anions in the water side of the interface. From an inspection of figure 3 it would appear that a change in temperature has no effect on the position of the first portions of the ascending branch of the curve. However, if these portions of the ascending branches are plotted on a larger scale, as shown in figure 5, it is observed that at the higher temperatures the interfacial tension values are higher. As the applied potential difference is increased the curves cross each other in such a manner that, at the higher temperatures, the interfacial tensions eventually become lower. This can be explained in the following manner (10). There are two factors operative. An increase in thermal agitation serves to lower the interfacial tension, and an increase in temperature decreases

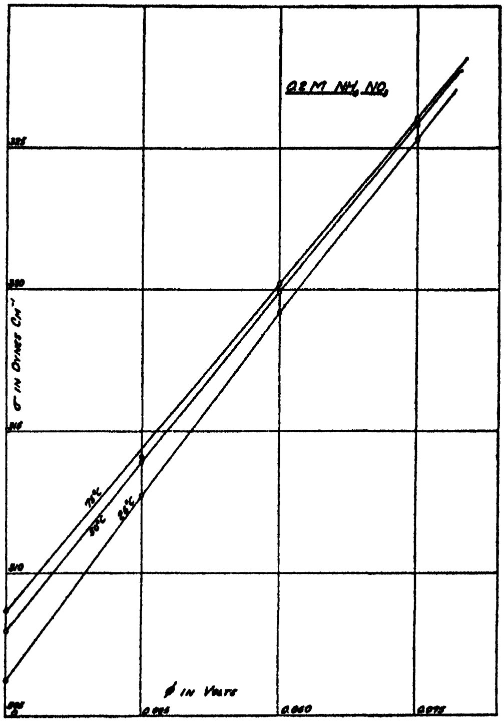

FIG. 5. ELECTROCAPILLARY CURVES FOR 0.2 *M* AMMONIUM NITRATE SOLUTION IN THE REGION OF THE ORIGIN OF THE CURVES AT 25°, 50°, AND 75°C.

the adsorption of mercury salt and acts to increase the interfacial tension. It is apparent that the effect of the adsorption is the more important one near the origin of the curves, but as the curves rise the effect of thermal agitation becomes more and more important and eventually causes reversal in the position of the curves.

The maximum

At the maximum of the electrocapillary curve the charge on the mercury should be zero, but Gouy (7) considered that additional ions will be present on the surface if they are capillary-active, so that at the maximum of the electrocapillary curve there may be still a considerable potential difference between the solution and the mercury due to this layer of capillary adsorbed ions. According to Freundlich (2), if the anions are capillary-active, the mercury must carry a negative charge at the maximum in order to balance the tendency of anion adsorption. In the same way, with capillary-active cations present the mercury must have a positive charge at the maximum.

It will be observed from an inspection of table 3 that the values of ϕ (max.) for the ammonium nitrate solutions become smaller as the temperature is increased. This is consistent with expectation and in agreement with the results published by Koenig (10) for potassium nitrate solutions. Formally, the situation may be discussed with the use of the equation,

$$\phi = \phi_{\text{ref.}} - \phi_P \qquad (1)$$

in which $\phi_{\text{ref.}}$ is the potential of reference, and ϕ_P may be described as the potential of the double layer at the polarized electrode. For the temperature variation of the maximum we have,

$$\frac{\partial\phi(\text{max.})}{\partial T} = \frac{\partial\phi_{\text{ref.}}}{\partial T} - \frac{\partial\phi_P}{\partial T} \qquad (2)$$

Contributions to ϕ_P result from the presence in the interface of ions and dipole molecules; in addition, the distribution of electrons and mercury ions in the charged surface of the metal itself is a factor.

At the present time it is impossible to determine ϕ_P and $\frac{\partial\phi_P}{\partial T}$ with any degree of accuracy, because the available methods for the estimation of $\phi_{\text{ref.}}$ and $\frac{\partial\phi_{\text{ref.}}}{\partial T}$ are not entirely satisfactory. But even if ϕ_P and $\frac{\partial\phi_P}{\partial T}$ could be determined, it would be a matter of extreme difficulty to separate the amounts contributed by the three factors,—ions, dipoles, and metal. For solutions of ammonium nitrate there are good reasons to believe the contributions of both ions and dipoles to be finite. In the maximum region of the curve the double layer at the interface contains some adsorbed anions. It also contains water molecules which are partially oriented in such a way that the negative end of the dipole is turned toward the mercury side of the interface. Now, since increasing temperature favors a decrease in the adsorption of anions and tends to increase the randomness of any effective orientation, a shift of the position of ϕ (max.) toward smaller values with increase in temperature is explained. As would be expected, the actual value of the interfacial tension decreases with increasing temperature and the entire curve is flattened out.

From the observed vertical shift of the maximum with concentration of added ammonium nitrate, calculations can be made for the surface densities at the maximum, Γ (max.), in equivalents per unit area (cm.^{2}), by using an equation of Gibbs. The chemical potential of the electrolyte, $\mu_{NH_4NO_3}$, is defined by the expression,

TABLE 5

Surface density data for ammonium nitrate solutions

T IN °C.	$\Gamma^{(max.)}_{NH_4NO_3}$ 1.0 *M* – 0.2 *M* NH_4NO_3	$\Gamma^{(max.)}_{NH_4NO_3}$ 0.2 *M* – 0.02 *M* NH_4NO_3
25	5.3×10^{-11}	1.0×10^{-11}
50	3.7×10^{-11}	0.7×10^{-11}
75	1.9×10^{-11}	0.6×10^{-11}

$$\mu_{NH_4NO_3} = \text{Const.} + RT \ln C_{NH_4^+} \cdot f_{NH_4^+} + RT \ln C_{NO_3^-} \cdot f_{NO_3^-}$$

Therefore,

$$d\mu_{NH_4NO_3} = 2\,RT \text{ d} \ln C_{NH_4NO_3} \cdot f_{NH_4NO_3} = 2\,RT \text{ d} \ln a_{NH_4NO_3}$$

The equation of Gibbs, in the form assigned it by Koenig (8), is

$$\frac{\partial\sigma(\text{max.})}{\partial\mu_{NH_4NO_3}} \cong -\Gamma^{(max.)}_{NH_4NO_3}$$

The numerical results of table 5 for $\Gamma^{(max.)}_{NH_4NO_3}$ have been obtained from graphs in which logarithms of ammonium nitrate activity were plotted as a function of the maximum interfacial tensions. The surface densities are seen to decrease with an increase in temperature and with a decrease in concentration. Also, since

$$\frac{\partial\sigma\ (\text{max.})}{\partial\mu_{NH_4NO_3}}$$

is negative, we may conclude that ammonium nitrate is a capillary-active electrolyte.

The descending branch

Along the descending branch the mercury side of the interface acquires a greater and greater negative charge and the anions are replaced by cations at the interface. In figure 3 it is observed that the descending branches of the electrocapillary curves are more or less uniformly displaced with a change in temperature. Higher temperatures lower the interfacial tension.

The effect of a change in concentration of ammonium nitrate on the position of the descending branch of the curve is shown in figure 2. As the concentration of the ammonium nitrate is lowered, the interfacial tension for equal values of applied potential increases. It was shown by Frumkin (4), and later by Koenig (8), that one can predict the effect of a change in concentration of the electrolyte on the shape of the electrocapillary curve. According to Gibbs there exists a simple relationship between the adsorbed quantity of a substance and the change of surface tension with concentration, which is expressed by the equation

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\sigma}{\mathrm{d}\ln a} \tag{3}$$

In this expression Γ is the excess of the solute in gram-moles per square centimeter of the dividing surface, a is the effective concentration or activity of the solute, and σ is the surface tension. Frumkin has shown that the equation for the electrocapillary curve can be written in the form,

$$\mathrm{d}\sigma = \epsilon \mathrm{d}\phi - \Sigma\Gamma_i \mathrm{d}\mu_i \tag{4}$$

where μ_i is the chemical potential of the i^{th} species present at the interface. It can be shown from equations 3 and 4 that

$$\left(\frac{\partial\phi}{\partial \ln a}\right)_\sigma = \frac{RT}{F}\frac{\Gamma_A + \Gamma_K}{n_A\Gamma_A - n_K\Gamma_K} \tag{5}$$

Here the subscripts A and K refer to the anion and cation, respectively, and n represents the valence of the ion. Along the descending branch of the curve only the cations are adsorbed at the interface, therefore the terms referring to the anions can be neglected, and we obtain the equation

$$\left(\frac{\partial\phi}{\partial \ln a}\right)_\sigma = \frac{RT}{n_K F}$$

When integrated between limits this equation gives

$$\phi_2 - \phi_1 = \frac{RT}{n_K F}\ln\frac{a_2}{a_1} \tag{6}$$

In a similar manner one obtains the following expression for the ascending branch.

$$\phi_2 - \phi_1 = \frac{RT}{n_A F} \ln \frac{a_2}{a_1} \qquad (7)$$

Equation 7 has not been applied with any degree of success because anions are usually capillary-active.

The application of equation 6 to the data for the ammonium nitrate solutions now can be illustrated. There are given in table 6 values calculated for the quantity $\frac{RT}{n_K F} \ln \frac{a_2}{a_1}$ at 25°, 50°, and 75°C., together with observed values of $\phi_2 - \phi_1$. The data may be considered to confirm the identity required by the equation.

TABLE 6

Electrocapillary data for 0.02 and 0.2 M ammonium nitrate solutions

AT 25°C.		AT 50°C.		AT 75°C.	
σ	$\phi_2 - \phi_1$	σ	$\phi_2 - \phi_1$	σ	$\phi_2 - \phi_1$
410	0.041	410	0.051	405	0.054
405	0.039	405	0.053	400	0.054
400	0.043	400	0.053	395	0.054
395	0.047	395	0.055	390	0.051
390	0.048	390	0.051	385	0.053
385	0.044	385	0.053	380	0.053
380	0.043			375	0.057
Average =	0.044	Average =	0.053	Average =	0.054
$\frac{RT}{F} \ln \frac{a_2}{a_1} =$	0.053	$\frac{RT}{F} \ln \frac{a_2}{a_1} =$	0.058	$\frac{RT}{F} \ln \frac{a_2}{a_1} =$	0.062

Activity coefficient data of Scatchard and Prentiss (12), obtained by the freezing point method, have been used in our calculations. It was necessary to assume these coefficients to be constant over the entire temperature range.

SUMMARY

1. A modified Lippmann electrometer was designed and built. With this apparatus electrocapillary curves were obtained for 1.0 molar, 0.2 molar, and 0.02 molar aqueous ammonium nitrate solutions at the temperatures 25°, 50°, and 75°C. The position of the maximum in each curve was located by means of an analytical procedure.
2. An explanation based upon the capillary activity of the ammonium

nitrate has been presented for the displacement of these curves toward lower values of interfacial tension with increase in temperature and with increase in concentration.

3. A displacement of the maxima of the curves toward lower values of applied potential at the higher temperatures has been partially accounted for on the basis of a decreased adsorption of anions and an increased tendency toward random distribution of solvent dipoles caused by the rise in temperature.

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OBSERVATIONS ON THE EFFECT OF MECHANICAL AGITATION ON ELECTRODE POTENTIAL[1]

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I. INTRODUCTION

The effect of mechanical agitation on the potential of an electrode immersed in an electrolyte solution is of interest because of its bearing on electrokinetics. In the experiments hitherto carried out on this effect the mechanical agitation has been produced in three different ways: (i) by moving the electrode (15, 6); (ii) by moving the electrolyte (3); (iii) by scraping the surface of contact between the electrode and the electrolyte with some suitable foreign body (2). In this note only the first two methods are considered.

The effect is conveniently described in terms of the quantity $\Delta\varphi$ given by

$$\Delta\varphi = \varphi_m - \varphi_r \tag{1}$$

where φ_r is the electric potential of the electrode with respect to the solution when the system is at rest, and φ_m the potential when the system is subjected to agitation. The quantity $\Delta\varphi$ can evidently be measured by means of a suitable reference electrode.

In recent years the quantities $\Delta\varphi$ have been extensively investigated for various metal electrodes in various electrolyte solutions by Stephan Procopiu (15, 16). This author does not describe his procedure in detail, but seems to have used method i exclusively, the electrode being attached to the armature of an electromagnetic vibrator. Procopiu's conclusions may be summarized by the equation

$$-\Delta\varphi \approx \zeta \tag{2}$$

where ζ is the electrokinetic potential of the electrode in the solution in question, defined in the usual manner. Equation 2 may be called the "electrokinetic theory" of the effect.

It is possible to account for equation 2 by making a number of assumptions as to the mechanism of the effect. Let that part of the double layer which, in the usual electrokinetic phenomena of electrosmosis etc., is displaced relative to the solid phase be called the mobile part; it extends from the "rigidity boundary" (12) out into the interior of the solution and contains a certain net electric charge, say $-\sigma$ coulombs $\times$ cm^{-2}. It is assumed (i) that the mobile part of the double layer is completely removed by the mechanical agitation, thereby removing $-\sigma$ coulombs $\times$ cm^{-2}. of charge from the liquid side of the rigidity boundary, (ii) that the electroneutrality (10) of what is left of the double layer is restored by the simultaneous disappearance of $+\sigma$ coulombs $\times$ cm^{-2}. from the solid side of the rigidity boundary. As a result the potential of the electrode with respect to the solution will be changed by an amount

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$$\Delta\varphi = \varphi_m - \varphi_r$$

which is such that σ and $-\Delta\varphi$ have the same sign (if $\sigma \lesseqgtr 0$, then $\Delta\varphi \gtreqless 0$). But from the definition of ζ it follows that σ and ζ have the same sign (if $\sigma \lesseqgtr 0$, then $\zeta \lesseqgtr 0$). Hence it follows from assumptions i and ii that ζ and $-\Delta\varphi$ have the same sign (if $\zeta \lesseqgtr 0$, then $\Delta\varphi \gtreqless 0$). Finally it is assumed (iii) that $-\Delta\varphi$ and ζ have also the same magnitude.[2] It is to be noted that the picture contained in assumptions i and ii implies that the effect is qualitatively of an entirely different kind from the usual electrokinetic effects, in which the mobile part of the double layer is not removed, but is displaced parallel to itself without disturbance of its average structure.

The validity of equation 2 is a question of some importance on account of the uncertainty (11) of the ζ values calculated from the usual electrokinetic measurements and the special difficulty of obtaining such measurements for metals. The uncertainty of the ordinary ζ values also makes it impossible to test equation 2 rigorously. Nevertheless, the best that can be done at the present time is to compare $\Delta\varphi$ and ζ for the same system, the ζ being obtained in the usual way. To this end Procopiu (16) has compared his $\Delta\varphi$ values for the metals platinum, silver, copper, bismuth, lead, and iron in water, with the ζ values obtained by Burton (5) from the electrophoretic velocities of colloidal particles of the same metals in water. For the metals silver and lead good agreement was found between $-\Delta\varphi$ and ζ, the metals platinum and iron agreed in sign but not in magnitude, and finally copper showed a discrepancy in both sign and magnitude. The deviations from equation 2 found here may be due to the fact that the colloidal metal particles, owing to their method of preparation, are in many cases covered with a layer of oxide or hydrated oxide (14). The comparison is therefore not decisive, and there are to the author's knowledge no other data available which could lead to a similar comparison. What evidence does exist for equation 2 is therefore even more incomplete than that obtainable from a comparison of the usual calculated ζ values with $\Delta\varphi$. This evidence may be summarized under three heads: (i) The observed $\Delta\varphi$ values are always of the same order of magnitude as the ζ values calculated from the usual electrokinetic data. (ii) For the metals silver, platinum, nickel, lead, iron, and zinc in water the sign of $-\Delta\varphi$ is the same as that of ζ as found by Burton (5) or by Coehn and Schafmeister (7). (iii) The curves obtained by Procopiu (16) for $\Delta\varphi$ as a function of the electrolyte concentration, c, have the same general shape as the familiar $\zeta - c$ curves (extrema, isoelectric points).

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[2] This picture of the electrokinetic theory of the effect differs in several features from that of Procopiu (16).

The chief purpose of this note is to suggest that the electrokinetic theory is not the only possible explanation of the effect, a reasonable alternative being the theory that irreversible chemical reactions at the electrode are partly or wholly responsible. The following observations lend support to this idea.

II. EXPERIMENTS

The electrodes used in the experiments were of pure soft silver wire about 1 mm. in diameter, of the sort used as anode in a silver coulometer. The mechanical agitation was produced both by causing the electrode to vibrate (method i) and by stirring the solution (method ii). The vibrating electrode was made by soldering a copper lead onto one end of a 4-cm. piece of the silver wire and then sealing the silver wire with DeKhotinsky cement into one end of a Pyrex tube 3 mm. in diameter and 8 cm. long, in such a way that about 2 cm. of the silver wire projected beyond the seal. The copper lead was passed out through a small hole blown through the wall of the glass tube near its other end, which was attached, also by means of deKhotinsky cement, to the arm of a vibrator made by sawing off the gong and the clapper from a small electric bell. Three such electrodes were prepared; they all gave the same results. Before use, the silver electrodes were always thoroughly polished first with dry rouge and filter paper and finally with dry filter paper alone to remove traces of the rouge.

The solution into which the electrode dipped was contained in a short-necked wide-mouthed 200-cc. flask. Dipping into the latter were, besides the vibrating electrode, a glass stirrer run by a small A.C. motor of 2000 R.P.M. and finally a glass siphon leading to another flask of the same solution, into which the snout of the reference electrode, a calomel electrode with 3.5 N potassium chloride, was immersed. With this arrangement the effects of vibrating and stirring could be studied side by side on the same system.

The potentials were measured with a Type K potentiometer in conjunction with a Leeds and Northrup HS galvanometer.

Preliminary experiments showed that only such solutions as enter into a fairly definite and reproducible electrochemical equilibrium with the silver give even approximately reproducible $\Delta\varphi$ values. Thus in an attempt to check Procopiu's (16) value, $\Delta\varphi = 15$ millivolts for silver in 0.2 N sulfuric acid, values were obtained lying anywhere between 6 and 30 millivolts depending on the length of time the electrode was allowed to remain immersed in the solution. Except where otherwise stated, the following experiments were carried out with potassium chloride solutions of various concentrations, saturated with silver chloride.

1. *Nature of the vibration effect in time*

A few minutes after the silver electrode is plunged into a potassium chloride solution saturated with silver chloride, it reaches a state in which its potential changes less than 0.0001 volt per minute and may be regarded as constant. If then the electrode is caused to vibrate, its potential *immediately* increases ($\Delta\varphi > 0$) to a new practically constant value which is maintained as long as the vibration lasts. On stopping the vibration the potential *gradually*, during the course of five to eight minutes, returns to the value before vibration. Figure 1, showing an experiment with 3.0 N potassium chloride, illustrates this behavior. $\Delta\varphi$ is always taken as the difference (with proper sign) between the steady values.

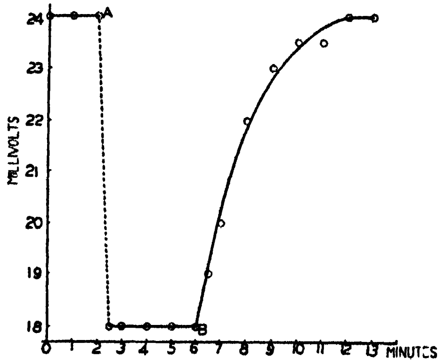

FIG. 1. E.M.F. OF THE CELL Ag|3.0 M KCl SATURATED WITH AgCl|3.5 N KCl SATURATED WITH HgCl|Hg, AS A FUNCTION OF THE TIME

A, vibration started; B, vibration stopped. The silver electrode is the negative pole, so that $\Delta\varphi>0$.

2. *Dependence of $\Delta\varphi$ on the frequency of the vibrator*

From the sound of the vibrator it was evident that its frequency increased with the voltage used to run it. Figure 2, in which the observed $\Delta\varphi$ for 1.0 N potassium chloride is plotted against the voltage applied to the vibrator, is typical of all the experiments with potassium chloride solutions and shows that $\Delta\varphi$ increases somewhat with the frequency, at least up to 6 volts. The application of 10 volts to the vibrator caused a sudden jump in frequency of two octaves. This increase in frequency in no case changed the $\Delta\varphi$ values appreciably from those obtained at 6 volts. This fact makes it probable that the $\Delta\varphi$ for 6 volts is practically a "saturation value." It is this "saturation value" which was always taken as the $\Delta\varphi$ of the system. For a potassium chloride solution of a given concentration the $\Delta\varphi$ so obtained is reproducible to ± 2 millivolts.

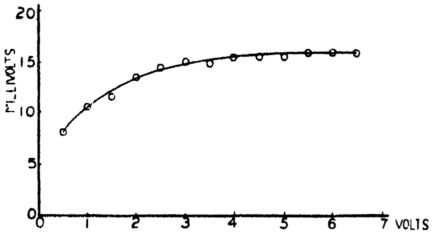

FIG. 2. $\Delta\varphi$ FOR 1 *N* KCl SATURATED WITH SILVER CHLORIDE, AS A FUNCTION OF THE VOLTAGE APPLIED TO THE VIBRATOR

TABLE 1

$\Delta\varphi$ values as a function of the potassium chloride normality

c, MOLES OF KCl PER LITER OF SOLUTION	$\Delta\varphi$
	millivolts
10^{-3}	27 ± 2
10^{-2}	25 ± 2
10^{-1}	32 ± 2
1.0	17 ± 2
3.0	6 ± 2

3. The $\Delta\varphi$ — c curve

Table 1 gives the $\Delta\varphi$ values obtained by vibration, as a function of the potassium chloride normality, *c*. Each of the $\Delta\varphi$ values is the average of nine experiments (three electrodes, three sets of solutions). Figure 3 shows $\Delta\varphi$ plotted against log *c*. Each of the five points is represented by a vertical line indicating the limits of reproducibility of $\Delta\varphi$ (± 2 millivolts). The curve has the general characteristics of the familiar $\zeta - c$ curves.

4. The effect of stirring

If the solution is stirred, as described above, an effect of the same sign as that produced by vibration of the electrode results. The $\Delta\varphi$ increases slightly with the rate of stirring, but the values obtained for the maximum rate of 2000 R.P.M. were 2 to 5 millivolts less, in the different solutions, than the maximum vibration values given in the above table.

5. *Effect of the removal of air*

The stirring experiment was carried out in an atmosphere of nitrogen as follows. Nitrogen from a tank was purified by passing it first through a strongly alkaline solution of sodium anthraquinone-β-sulfonate and sodium hyposulfite, then over dry calcium chloride, and finally over copper gauze at a dull red heat. An apparatus was set up in which the potassium chloride–silver chloride solutions to be investigated could be boiled and cooled while the pure nitrogen was bubbled through them, and then forced into a stoppered flask, previously filled with nitrogen and containing a glass stirrer introduced through an air-tight mercury seal, a silver electrode, and a siphon to the reference electrode. It was found that stirring gave $\Delta\varphi$ values of the same magnitude as in the presence of air, but that when, after conclusion of the experiment in nitrogen, air was bubbled through the solutions, the potential φ_r of the silver electrode at rest increased by 3 to 5 millivolts. That is, the $\Delta\varphi$ effect persists when the air is replaced by nitrogen, but the silver electrode at rest is more positive in the presence of air than of pure nitrogen.

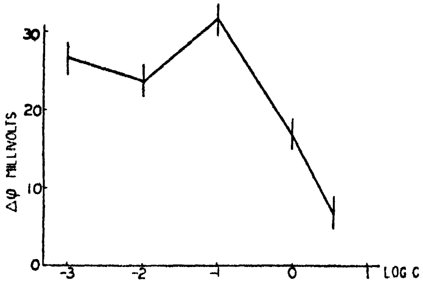

FIG. 3. $\Delta\varphi$ FOR KCl SOLUTIONS SATURATED WITH SILVER CHLORIDE, AS A FUNCTION OF THE LOGARITHM OF THE POTASSIUM CHLORIDE NORMALITY, c

6. *Effect of sodium bisulfite*

The addition of 1 g. of sodium bisulfite to 100 cc. of potassium chloride solution caused the complete disappearance of the effect in solutions of all concentrations up to 3 *N*.

7. *Silver nitrate solutions*

Finally, the effect of vibration and stirring was investigated with the silver electrodes immersed in silver nitrate solutions. It was found that $\Delta\varphi = 0$ for silver nitrate concentrations between 10^{-3} *N* and 1 *N*.

III. DISCUSSION

The above observations can all be qualitatively explained either by the electrokinetic theory described above or by the following "chemical theory." It is assumed that the silver immersed in potassium chloride solutions saturated with silver chloride tends towards electrochemical equilibrium not only with respect to the Ag^+ ions:

$$Ag^+ \text{ (metal)} \rightleftharpoons Ag^+ \text{ (solution)}$$

but also with respect to the dissolved oxygen:

$$4OH^- \text{ (solution)} \rightleftharpoons 2H_2O \text{ (solution)} + O_2 \text{ (solution)} + 4\ominus \text{ (metal)}$$

i.e., the silver metal functions also as an oxygen electrode, and is therefore the more positive the greater the concentrations of dissolved oxygen in its immediate neighborhood. It is furthermore assumed that the following irreversible chemical reaction:

$$\begin{aligned} 4Ag \text{ (metal)} + 4H^+ \text{ (solution)} + 4Cl^- \text{ (solution)} + O_2 \text{ (solution)} \\ = 4AgCl \text{ (solid)} + 2H_2O \text{ (solution)} \end{aligned}$$

is always proceeding slowly at the metal surface. This reaction tends to decrease the concentration of dissolved oxygen in the immediate neighborhood of the electrode. Vibrating and stirring aid diffusion and therefore keep the oxygen concentration closer to its value in the bulk of the solution, thus producing a positive $\Delta\varphi$.

That an oxygen electrode effect is present at the silver surface in potassium chloride solutions saturated with silver chloride is rendered fairly certain by observation 5 above, that the electrode is more positive in the presence of air than of pure nitrogen. That $\Delta\varphi$ nevertheless persists after boiling out the solutions in a current of pure nitrogen may be due to the fact that it is impossible to remove dissolved oxygen completely by this method. Sodium bisulfite, on the other hand, is known to remove the last traces of oxygen from a solution, so that the chemical theory is confirmed by observation 6.

When the silver-ion concentration is appreciable compared with the concentration of dissolved oxygen, the effect of the latter on the electrode potential is negligible compared with that of the former. The chemical theory therefore predicts $\Delta\varphi = 0$ for silver nitrate solutions of moderate concentrations, in accordance with observation 7. In this connection it is to be noted that Henry (9), using the method of the deflection of thin wires in an electric field, found practically zero deflection for the system silver–silver nitrate, but whether this means that ζ is really zero or merely that the specific conductivity of the wire is large compared with that of the solution (1) is not certain.

Regarding the effect of stirring (observation 4), it is to be noted that this effect implies a conflict between the electrokinetic theory of $\Delta\varphi$ and the generally accepted ideas as to the kinetics of heterogeneous reactions. According to the latter, there is generally at the surface of a solid in contact with a solution an unstirrable liquid film (4, 8, 13). If this is true, then the mobile part of the double layer cannot, as demanded by the electrokinetic theory, be removed by stirring, and $\Delta\varphi$ should be zero. From the point of view of the chemical theory there is evidently no conflict of this sort.

Regarding observation 1, it may be noted that practically nothing is known regarding the time necessary for the formation of the mobile part of the double layer. It is no doubt greater than the time required for the formation of an ionic atmosphere ("relaxation time"), which is of the order of $\frac{10^{-10}}{c}$ seconds. But that it should be a matter of minutes seems improbable. The time effect shown in figure 1 would therefore seem to favor the chemical rather than the electrokinetic theory.

It is of course possible that the observed effects result from an overlapping of electrokinetic and chemical processes rather than from either kind of process alone. Finally, it is worth mentioning that the idea that chemical reactions involving dissolved gases are at least partly responsible for $\Delta\varphi$ is strongly supported by the observations of Charmandarjan and Peruschwin (6), who studied the electric current which flows from a platinum electrode agitated in a solution of sulfuric acid, hydrochloric acid, nitric acid, oxalic acid, or phosphoric acid to another platinum electrode at rest in the same solutions. It was found that the magnitude and, for hydrochloric acid, even the sign of the current is different depending on whether or not the solution has been subjected to electrolysis before the measurement.

IV. SUMMARY

The electrokinetic theory of the effect of mechanical agitation upon electrode potential is critically discussed. It is pointed out that this theory is not the only possible explanation, an alternative being the theory that irreversible chemical processes are partly or wholly responsible for the effect. Experiments with silver electrodes in potassium chloride solutions saturated with silver chloride and in silver nitrate solutions are described which lend support to the chemical theory of the effect.

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ELECTROKINETIC POTENTIAL OF SILVER IODIDE

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I. INTRODUCTION

It might be assumed that the electrokinetic potential of halogen salts of silver against pure water would be zero. However, Labes (8), Mukherjee and Kundu (12), Kruyt and Van der Willigen (7), Lange and Crane (9), and Basinski (3) have shown that the electrokinetic potential, ζ, of these salts (in particular, silver iodide) at the point of equivalence, i.e., at equal concentrations of silver and of halogen ions in solution, has a rather considerable negative value. Zero value of the electrokinetic potential was attained only by having a rather considerable excess of silver ions in solution. At higher concentrations of the soluble silver salt the silver halide is charged positively, but on subsequent dilution of the solution with water the potential falls to lower values and finally becomes negative.

This phenomenon is not confined to silver halides. Lottermoser and Riedel (10) consider the negative charge in pure water to be proper to all substances and confirmed this with many examples.

Labes, Mukherjee and Kundu, as well as Lange and Crane, measured the potential by the rate of the endosmosis, that is, on the boundary of the coarsely dispersed silver halide, while only the last authors measured systematically the whole curve of the dependence of ζ-potential of silver iodide on the concentration of the excess ion constituting the lattice of the salt (silver ion or iodide ion). In other researches electrophoresis of sols was used, but the data obtained were either only approximate or concerned with the influence of the dilution with water on the ζ-potential of the positively charged sol, i.e., the simultaneous change and concentration of the electrolyte and the concentration of the dispersed substance.

My aim has been to measure the curve ζ-potential–concentration of electrolyte, similar to that one obtained by Lange and Crane, but with sols of highly dispersed silver iodide.

II. METHOD OF ζ-POTENTIAL DETERMINATION

ζ-potentials were determined by rate of the electrophoresis of sol observed through an ultramicroscope. The method was that of P. Tuorila (14). Observations were made with the help of the slit ultramicroscope of

C. Zeiss. The cell used was pasted together by means of picein; it contained two platinum electrodes and a tightly fitting glass cover.

The distance between the electrodes was 35 mm., and the depth of the cell 5 mm. On the upper side of the cell a slight scratch was made with a diamond. The cell was set on the vertically displaceable stage of the microscope, and the latter was focused first on the scratch and then on the illuminated layer of sol. If the displacement of the microscope tube, *D*, is known as well as the true thickness of the glass plate, *d*, then the thickness of the layer of liquid between the inner surface of the upper glass and the plane under observation will be as follows:

$$x = \frac{n_1}{n_2}D - \frac{d}{n_2}$$

where n_1 and n_2 are the refractive indices at the interfaces glass–exterior medium and glass–sol. Since the objective was used with water immersion, we may put $n_1 - n_2 = n_{H_2O}$

$$x = D - \frac{d}{n_{H_2O}}$$

where $\frac{d}{n_{H_2O}}$ = the optical thickness of the plate, is established.

The observed velocity of electrophoresis of the dispersed phase at different distances from the walls of the cell is the algebraic sum of the true velocity and of that of endosmose of the solution relative to the walls of the cell.

According to Smoluchovsky (13) the velocity of endosmose in the closed cell at the distance x from one of the two parallel sides distant l apart is:

$$U_x = U_0\left[1 - 6\left(\frac{x}{l} - \frac{x^2}{l^2}\right)\right]$$

where U_0 is the velocity of endosmose close to a side. The rate of motion of the particles observed by the ultramicroscope is equal to velocity of electrophoresis, *v*, at the depth where $U_x = 0$, i.e., when

$$\frac{x}{l} = \frac{1}{2} \pm \frac{1}{2\sqrt{3}}$$

or $x_1 = 0.211l$ and $x_2 = 0.789l$.

The parabolic curve of Smoluchovsky's function near this "neutral layer" is nearly a straight line. Hence, by measuring the velocity of motion of particles in the electric field, once at a depth somewhat smaller and then at one greater than $0.211l$, it is possible to find the true velocity of electrophoresis, *v*, by interpolation.

A difference of potentials of about 12 volts was applied to the electrodes, about 3.5 volts per centimeter. By means of a stop watch the time of passing of the observed particle between two selected divisions of the ocular-micrometer was measured, first in the field, where the positive pole was on the left, second, in the case of short-circuited electrodes (for in a wide cell there are always curious, partly convectional currents of liquid, more or less constant in velocity), and lastly in the reversed field. Measurements of this kind were repeated at both depths four to seven times.

The potential was calculated with the usual equation for spherical particles, due to Debye and Hückel:

$$\zeta = \frac{6\pi\eta}{HD} v$$

where η is the viscosity, taken as the viscosity of pure water, H is the potential gradient, and D is the dielectric constant, considered equal to 81.

Sols were prepared in the following way. To 37.5 cc. of the solution of one of the electrolytes (potassium iodide or silver nitrate) during exactly 3 minutes and with constant stirring, 12.5 cc. of the second electrolyte was added. The mixture was made in yellow light. The sol was violently shaken and left standing for three to four hours in order to attain a state of comparative equilibrium. After that the ζ-potential was measured.

Two series of experiments were undertaken with three different concentrations of silver iodide in each, viz., $M/400$, $M/4000$, and $M/20{,}000$.

These two series were made at different times and differed from each other by the following conditions: (1) In the first series common distilled water was used, while the water used for the second series was carefully distilled three times through a silver condenser. (2) In the first series, sols were made in such a way that the first solution (37.5 cc.) contained that electrolyte of which there was an excess, while in the second series that electrolyte was used one of the ions of which communicated the charge to sol, which fact was discovered from the results of the first series.

Experiments showed that the potential did not change with time.

$M/4000$ AgI, 10^{-5} M KI	After 2 hours	= −50 mv.
	After 48 hours	= −56 mv.
$M/400$ AgI, 10^{-4} M $AgNO_3$	After 3 hours	= +38 mv.
	After 48 hours	= +37 mv.
$M/20{,}000$ AgI, 10^{-4} M $AgNO_3$	After 3 hours	= −25 mv.
	After 24 hours	= −26 mv.
$M/400$ AgI, 10^{-5} M KI	After ¼ of an hour	= −45 mv.
	After 5½ hours	= −48 mv.

III. POTENTIALS OF SOLS WITH DIFFERENT CONCENTRATIONS OF SILVER IODIDE

The results of measurements made during the *first* series of experiments are shown in table 1. Several values in one column correspond to the potentials of sols made up at different times; these data give an indication of the reproducibility of the experiments.

It should be noted that sols with the contents of *M*/10 potassium iodide are already of great electrical conductivity, and consequently the data obtained are approximate.

TABLE 1

Potentials of sols with different concentrations of silver iodide

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
		Concentration of AgI in sol		
$AgNO_3$	KI	$\frac{M}{400}$	$\frac{M}{4000}$	$\frac{M}{20{,}000}$
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv.*	*mv.*
10^{-2}		+58	+49, +44	+32
10^{-3}		+55	+21, +36	+12, −2
10^{-4}		+38	+15	+25
$10^{-4.2}$		—	+1	—
10^{-5}		0	−16, −13, −35	−31, −36
10^{-6}		—	−53	−43
10^{-8}	10^{-8}	—	—	−53
	10^{-6}	—	−48	−56
	10^{-5}	−44	−60, −50	−50, −50
	$10^{-4.2}$	—	−62	—
	10^{-4}	−50	−51	−50
	10^{-3}	−44	−53	−53
	10^{-2}	−55	−73	−65, −49
	$10^{-1.2}$	—	approx. −100	—
	10^{-1}	approx. −170	—	approx. −105

ζ-potentials of the *second* series of experiments are given in table 2.

Basinski (3) for the more concentrated sol (*N*/50 silver iodide) obtained the following values of ζ-potential:

	ζ-potential
At 10^{-2} *M* $AgNO_3$	= +46.9 mv.
At 10^{-3} *M* $AgNO_3$	= +47.3 mv.
At 10^{-2} *M* KI	= −70.1 mv.

i.e., values coinciding practically with those which refer to our *M*/400 sol. The results are shown graphically in figures 1 and 2.

The more the sol is diluted, the greater is the difficulty in charging it

TABLE 2

Potentials of sols with different concentrations of silver iodide

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
		Concentration of AgI in sol		
$AgNO_3$	KI	$\frac{M}{400}$	$\frac{M}{4000}$	$\frac{M}{20,000}$
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv.*	*mv.*
10^{-2}		+50	+58	+30
10^{-3}		+43	+37	+10
10^{-4}		+45, +41	+38	−10
10^{-5}		0 (?)	+20, 0	−24
10^{-6}		−	−29	−40
10^{-8}	10^{-8}	−23	−	−
	10^{-6}	−	−	−33, −37
	10^{-5}	−48, −45, −46	−43	−32
	10^{-4}	−36	−41	−39
	10^{-3}	−37	−47	−49
	10^{-2}	−69	−75	−71
	10^{-1}	approx. −135	approx. −115	−

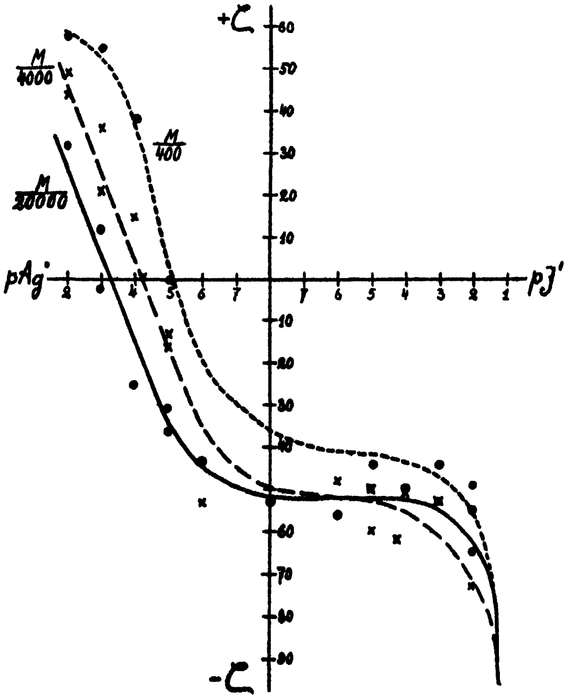

FIG. 1

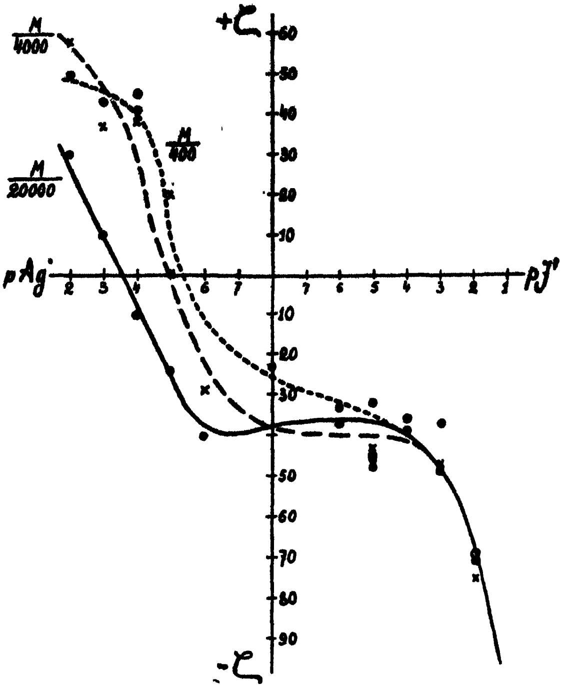
+ζ
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
-ζ
M/4000
M/400
M/20000
pAg'
2
3
4
5
6
7
7
6
5
4
3
2
1
pJ'

Fig. 2

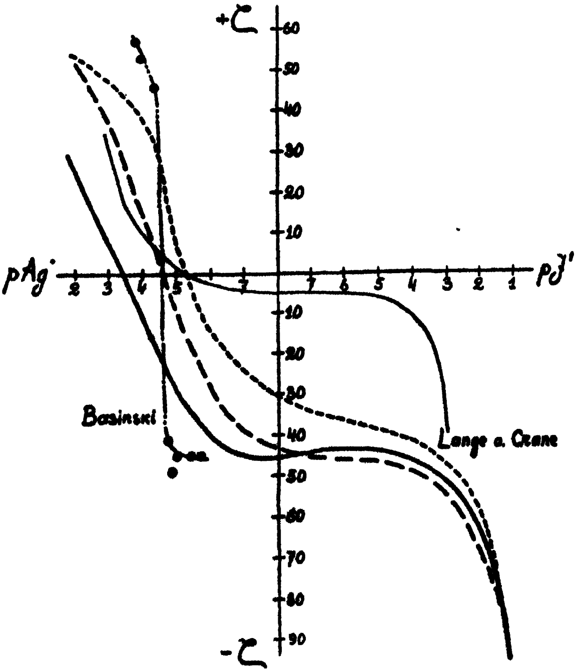
+ζ
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
-ζ
pAg'
2
3
4
5
7
7
6
5
4
3
2
1
pJ'
Basinski
Lange a. Crane

Fig. 3

positively and the less is its ζ-potential in the region of positive charge. Accordingly the isoelectric point ($\zeta = 0$) is shifted; if in the case of the sol of $M/400$ silver iodide, the concentration of silver ion exceeds at this point the concentration of iodide ion by 10^6, then in the case of the sol with content of silver iodide fifty times less, the concentration of silver ion exceeds the concentration of iodide ion by 10^9. Outwardly this change is manifested by a quite obvious shift of the domain of minimum stability of the sols.

The curves obtained differ to a great extent from the endosmotic curve of Lange and Crane (see figure 3, where the average curves of both series of tests are shown).

While it is possible to explain fully this last divergence by the difference of the methods of measurement and by the fact that the conditions of adsorption of ions on silver iodide in statu nascendi can differ considerably from the adsorption on the precipitate previously made, the divergence between the potential curves of sols of dissimilar concentrations requires a special explanation.

IV. INFLUENCE OF DILUTION UPON ζ-POTENTIAL

It may be supposed that ζ-potential depends on the conditions of preparation of the sol. The more the initial solutions are diluted, the larger would be the particles and the less the relative quantity of adsorbed silver ions, which according to Kruyt's view (6) are adsorbed chiefly on the edges of the crystals. Endosmotic experiments of Kruyt showed that fused silver iodide differed from precipitated since it was not possible to charge it positively even with high concentrations of silver nitrate. The possibility indicated is not peculiar to heteropolar crystals, but also occurs with noncrystalline spherical particles. The dependence of the velocity of transference (and consequently of ζ-potential) on the radius was established by means of experiment. Illig and Schönfeld (5) have observed this by the endosmose of water through diaphragms with pores of different size; Mooney (11) with emulsions of oil in water; Alty (1) with bubbles of gas in water. In later researches this dependence is expressed mathematically (2, 4).

In connection with such hypotheses it is interesting to compare the results obtained with phenomena found in the usual dilution of sols.

Basinski[1] showed that there is no marked influence of dilution by ultrafiltrate on the ζ-potential of the positively charged sol, but the same dilution of the negatively charged sol leads to a decrease of the potential. The dilution with water of the positively charged silver iodide sol gives a sharper curve for ζ-potential than that in our work. But it is necessary to take into consideration that the reduction of concentration of excess electrolyte and that of the dispersed phase take place simultaneously on dilution with water; thus, the positive potentials (concentration of silver iodide from $M/1250$ to $M/5000$) belong to sols which approach the most concentrated of my sols, and negative potentials (concentration of silver iodide from $M/10{,}000$ to $M/100{,}000$) belong to sols which are for the most part more diluted than the least concentrated of my sols. Under such circumstances I consider that the data given by this author confirm the presence of a concentration dependence of ζ-potentials of sols.

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[1] Reference 3, pp. 332–9. The curve in our figure 4 is drawn from table 44.

In order to verify these results, I also made experiments on the dilution of the sol of $M/400$ silver iodide by means of isoelectrolytic solutions, that is, by solutions containing the same quantity of excess electrolyte as the initial sol, and also by means of solutions which contained excess electrolyte with $M/250$ potassium nitrate (see table 3). It is difficult to suppose that this electrolyte influences the ζ-potential, but as it was being formed in dissimilar quantities in sols of different concentrations of silver iodide, it was necessary to take this fact into consideration.

TABLE 3

Potentials obtained after dilution of the M/400 silver iodide sol

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
$AgNO_3$	KI	$M/400$ sol AgI	The same but diluted to $M/20{,}000$ AgI	Diluted sol with $M/250$ KNO_3
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv*	*mv.*
10^{-2}		+56	+30	+27
10^{-3}		+49	+13	+16
10^{-4}		+41	+8	+10
10^{-5}		+23	−23, −28	−27
10^{-6}	10^{-6}	−53 (?)	−26, −32	−22
	10^{-5}	−55	−40	−49
	10^{-4}	−51	−52	−39
	10^{-3}	−51	−56	−51
	10^{-2}	−82	−71	−70
	10^{-1}	approx. −145	approx. −120	—

It follows from these data that simple dilution of the sol gives exactly the same general results as have already been observed: the diluted sol has a smaller positive charge than the concentrated sol, and the isoelectric point is shifted from the point of equivalence. The presence of potassium nitrate has practically no effect on the value of the ζ-potential. Therefore the conditions of preparing a sol do not cause a dependence of ζ-potential on the concentration of the dispersed phase.

It seemed possible to explain the results otherwise. The fact that the flocculation value depends on the concentration of sol is generally explained in the following way: the higher the concentration of dispersed phase, the greater will be the proportion of the dissolved electrolyte which partakes in adsorption and the less the equilibrium concentration of electrolyte as compared with the initial concentration. But in our case this reasoning leads to conclusions contrary to experiment.

V. pH OF SOLS OF SILVER IODIDE

Let us examine the problem of the structure of the double electric layer of silver iodide. The rule by Paneth-Fajans states that those ions are adsorbed on the surface of the heteropolar crystal which give, together with the oppositely charged ions of the crystal lattice, the least soluble compounds. We suppose that the "composition" of the second layer of the double layer is also determined by this rule, i.e., that the latter layer is formed for the most part from ions which give together with ions of the first layer the least soluble compounds.

TABLE 4

Results of pH measurements

EXCESS CONCENTRATION OF SILVER ION	CONCENTRATION OF DISPERSED AgI				
	$M/400$		$M/20,000$		0
	The made up sol	Centrifuging	The made up sol	Dilution of sol $M/400$	
10^{-2} M		6.05	6.13	6.38	
0					5.70
10^{-3} M	5.17		5.32	5.27	
10^{-3} M	5.83	5.80		5.73	5.83
0					5.16
10^{-4} M		6.68	6.25	6.31	6.40
10^{-5} M	6.31	6.27			
0					5.41

In the case of negatively charged silver iodide sol, iodide ions constitute the first layer; it is evident that potassium and hydrogen ions can form the second diffuse layer. In positively charged sols silver ions constitute the first layer and either nitrate or hydroxyl ions constitute the second layer. According to what precedes, in the case of the positively charged sol hydroxyl ions form chiefly the second layer, as silver hydroxide is but slightly soluble. In this case the equilibrium $H^+ + OH^- \rightleftarrows H_2O$ is displaced and the intermicellar liquid is slightly acid. The higher the concentration of dispersed phase, the more the liquid will be acidified. In compliance with the decrease of concentration of "free" hydroxyl ion, the relative amount of hydroxyl ion in the diffuse layer will be less in the concentrated sol than in the diluted one. The layer will be more diffused and the value of the ζ-potential will increase.

In order to verify such an hypothesis, the pH values of sols were measured by means of a glass electrode. The determinations with positively charged sol were rather difficult, since the more positive the sol, the more intensely it was precipitated on the negatively charged glass and on the film of the electrode as well. In consequence, the potential proved to be unstable and badly reproducible (3 to 5 millivolts, and sometimes more).

Table 4 gives the results of the pH measurements made at different times. They give generally a negative answer to our problem.

However, the negative results do not exclude the possibility of such an explanation of the phenomenon. Ions constituting the diffuse layer of the double electric layer can be active in regard to the glass electrode, and then the value of pH will tell us nothing of the structure of the double layer.

VI. SUMMARY

1. Electrokinetic potentials of sols of silver iodide with $M/400$, $M/4000$ and $M/20,000$ silver iodide made in different excesses of ions (silver or iodide) were electrophoretically measured.

2. The curves ζ–$C_{\text{electrolyte}}$ of silver iodide sols do not coincide with the curve in the case of endosmose through the precipitate (Lange and Crane).

3. The less the concentration of the dispersed phase in sols, the greater are the concentrations of silver ion necessary to charge it positively and the further the isoelectric point is removed from the point of equivalence in the direction of the excess of silver ions.

4. The dilution of sol $M/400$ silver iodide by means of solutions containing the same quantities of excess electrolyte as the initial sol leads also to decrease of positive charge of the sol.

5. The alteration of the concentration of dispersed phase does not cause any change of pH of the sols.

I wish to express my deepest gratitude to Mr. K. S. Ljalikov, to whose initiative this work was due and who invariably gave it his closest attention.

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TEMPERATURE VARIATION OF IONIZATION CONSTANTS IN AQUEOUS SOLUTIONS

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According to Harned and Embree (5), the temperature variation of the ionization constant can, as a first approximation, be represented by a quadratic equation of the type

$$\log K - \log K_m = -p(t - \theta)^2 \tag{1}$$

where K is the ionization constant, K_m is the maximum value of the ionization constant, p is a *general* constant and has a value of 5.0×10^{-5} deg.$^{-2}$, t is the Centigrade temperature, and θ is the temperature at which K is equal to K_m. For purposes of theoretical significance to be used later in connection with van't Hoff's isochor and the temperature variation of the heat of reaction, the temperature may be expressed in degrees Absolute without changing the value of p. Equation 1 then becomes

$$\log K - \log K_m = -p(T - \theta_1)^2 \tag{2}$$

where T is the absolute temperature and θ_1 is the absolute temperature at which K is equal to K_m. Thus, log K may be expressed by a quadratic equation

$$\log K = (\log K_m - p\theta_1^2) + 2p\theta_1 T - pT^2 \tag{3}$$

in which K_m and θ_1 are constants characteristic of each substance, and the constant p is general.

Likewise, equation 1 becomes

$$\log K = (\log K_m - p\theta^2) + 2p\theta t - pt^2 \tag{4}$$

By rearranging terms, equations 3 and 4 become, respectively,

$$\log K + pT^2 = \log K_m - p\theta_1^2 + 2p\theta_1 T \tag{5}$$

and

$$\log K + pt^2 = \log K_m - p\theta^2 + 2p\theta t \tag{6}$$

It is the object of this paper to show that p is not a characteristic constant except under certain assumptions. The theoretical significance of p and its relation to $d^2 \log K/dT^2$ will also be pointed out.

By taking the first derivative of log K with respect to temperature in equation 1:

$$\frac{d \log K}{dT} = -2p(t - \theta) \tag{7}$$

Likewise, from equation 2:

$$\frac{d \log K}{dT} = -2p(T - \theta_1) \tag{8}$$

But from van't Hoff's isochor,

$$\frac{d \log K}{dT} = \frac{\Delta H}{2.303RT^2} \tag{9}$$

where ΔH is the heat of reaction, or in this case, the molal heat of ionization.

By taking the second derivative of equation 1,

$$\frac{d^2 \log K}{dT^2} = -2p \tag{10}$$

Likewise, by differentiating equation 9:

$$\frac{d^2 \log K}{dT^2} = \frac{d(\Delta H)}{2.303RT^2\, dT} - \frac{2\Delta H}{2.303RT^3} \tag{11}$$

but

$$\frac{d(\Delta H)}{dT} = \Delta C_p \tag{12}$$

where ΔC_p is the change in specific heat upon ionization. Therefore

$$\frac{d^2 \log K}{dT^2} = \frac{\Delta C_p}{2.303RT^2} - \frac{2\Delta H}{2.303RT^3} \tag{13}$$

If the variation of log K with temperature is not originally expressed as a quadratic equation, and if ΔH and ΔC_p are not calculated from this quadratic equation, the validity of the assumption, namely, that p is a *general* constant, may be tested by combining equations 10 and 13:

$$-2p = \frac{\Delta C_p}{2.303RT^2} - \frac{2\Delta H}{2.303RT^3} \tag{14}$$

and dividing by 2,

$$-p = \frac{\Delta C_p}{4.606RT^2} - \frac{\Delta H}{2.303RT^3} \tag{15}$$

Equation 15 may be tested in two ways. Since $\Delta H = 0$ somewhere at or near the temperatures under consideration, one may determine the value of $-p$ at $\Delta H = 0$. This value will be the value of $-p$ at $\log K_m$ because $\frac{\mathrm{d} \log K}{\mathrm{d}T} = \frac{\Delta H}{RT^2}$ and at K_m, $\Delta H = 0$. Equation 15 then becomes

$$\frac{\Delta C_p}{4.606RT^2} = -p \tag{16}$$

Table 1 shows the values of $-p$ at K_m found in the literature. It shows that $-p$ does not have a constant value of 5.0×10^{-5} as was assumed by Harned and Embree (5).

In order to determine if $-p$ remained constant for any particular acid through a range of temperatures, equation 15 was applied to the series of acids in table 1. The constants used and the results calculated for these acids are given in table 2.

TABLE 1

The value of $-p$ at K_m

SUBSTANCE	ΔC_p	T	$-p = \frac{\Delta C_p \times 10^5}{4\ 606RT^2}$
Formic acid (4)	−41 0	298	5 06
Chloroacetic acid (9)	−48 9	269	7 38
Acetic acid (2)	−33 7	295	4 23
Propionic acid (3)	−37 1	293	4 72
Glycine (K_A) (8)	−45 0	328	4 57
Alanine (K_A) (7)	−23.2	321	2 46
Phosphoric acid (second hydrogen) (6)	−41 0	316	4.50
Sulfuric acid (second hydrogen) (1)	−74 5	269	11.25

Table 2 shows that p is not a constant, characteristic of any particular acid, unless the variation of $\log K$ with temperature is originally expressed as a quadratic equation. It was observed that p increased with temperature except where $\log K$ had been expressed as a quadratic function. Figure 1 shows that equation 13 will have a point of inflection at some temperature above that of the experiment. This fact cannot be true if $\log K$ is expressed as a general quadratic equation, as illustrated by lines II and III of figure 1.

At the point of inflection, $\frac{\mathrm{d}^2 \log K}{\mathrm{d}T^2} = 0$ and equation 13 becomes

$$\frac{\Delta C_p}{2.303RT^2} = \frac{2\Delta H}{2.303RT^3} \tag{17}$$

which, upon simplification, becomes

$$\Delta C_p = \frac{2\Delta H}{T}\ . \tag{18}$$

TABLE 2

Variation in ΔH and ΔC_p with temperature

TEMPERATURE	ΔH	ΔC_p	$\frac{\Delta C_p \times 10^5}{4.606RT^2}$	$\frac{\Delta H \times 10^5}{2.303RT^3}$	$-p \times 10^5$	$\frac{\Delta H \times 10^3}{2.303RT^2}$
			Propionic acid			
273	737	−34.7	−5.090	0.792	5.88	2.162
278	562	−35.3	−4.993	0.572	5.57	1.590
283	384	−35.9	−4.900	0.370	5.27	1.048
288	203	−36.5	−4.811	0.186	5.00	0.535
293	19	−37.1	−4.724	0.017	4.74	0.048
298	−168	−37.7	−4.652	−0.139	4.51	−0.415
303	−358	−38.3	−4.561	−0.282	4.28	−0.853
308	−551	−38.9	−4.483	−0.412	4.07	−1.270
313	−746	−39.4	−4.397	−0.532	3.87	−1.665
318	−945	−40.0	−4.324	−0.643	3.68	−2.043
323	−1147	−40.6	−4.254	−0.744	3.51	−2.404
328	−1351	−41.2	−4.187	−0.837	3.35	−2.746
333	−1559	−41.8	−4.121	−0.923	3.20	−3.074
			Chloroacetic acid			
273	−149	−46.83	−6.869	−0.160	6.71	−0.368
283	−593	−42.04	−5.738	−0.572	5.17	−1.619
291	−914	−38.21	−4.933	−0.811	4.12	−2.360
298	−1170	−34.86	−4.301	−0.967	3.33	−2.821
305	−1402	−31.51	−3.703	−1.080	2.62	−3.295
313	−1639	−27.68	−3.089	−1.169	1.92	−3.658
			Glycine (K_A)*			
283	1562	−23.4	−3.194	1.507	4.70	4.264
288	1439	−25.8	−3.400	1.317	4.72	3.793
293	1305	−28.2	−3.591	1.134	4.73	3.324
298	1159	−30.6	−3.776	0.958	4.73	2.860
303	1000	−33.0	−3.930	0.786	4.72	2.382
308	829	−35.4	−4.079	0.623	4.70	1.911
313	646	−37.8	−4.218	0.461	4.70	1.442
318	449	−40.2	−4.346	0.305	4.65	0.971
			Acetic acid			
273	714	−32.15	−4.716	0.767	5.48	2.095
278	552	−32.50	−4.597	0.562	5.16	1.562
283	389	−32.85	−4.484	0.375	4.86	1.062
288	223	−33.20	−4.376	0.204	4.58	0.588
293	57	−33.55	−4.272	0.050	4.32	0.145
298	−112	−33.91	−4.184	−0.093	4.09	−0.276

* ΔC_p was calculated from Owen's equation, $d(\Delta H)/dt = 18.6 - 48t$. It was observed that log K was expressed as a quadratic function. Calculation of ΔH and ΔC_p from a quadratic equation in t must necessarily produce a constant value of p by this method, because the coefficient of the square term is p. Values from log K_B for glycine were not computed because log K_B had been expressed as a quadratic function of temperature.

TABLE 2—*Concluded*

TEMPERATURE	ΔH	ΔC_p	$\frac{\Delta C_p \times 10^5}{4.606RT^2}$	$\frac{\Delta H' \times 10^5}{2.303RT^3}$	$-p \times 10^5$	$\frac{\Delta H \times 10^3}{2.303RT^2}$
			Acetic acid—*Concluded*			
303	−282	−34.26	−4.080	−0.222	3.86	−0.672
308	−455	−34.61	−3.988	−0.342	3.65	−1.049
313	−628	−34 96	−3.901	−0.448	3.45	−1.402
318	−804	−35.31	−3 817	−0.547	3.27	−1.738
323	−982	−35.66	−3.737	−0.637	3.10	−2.058
328	−1161	−36.02	−3.660	−0.736	2.92	−2.360
333	−1342	−36.37	−3.586	−0.795	2.79	−2.646
			Formic acid			
273	931	−34.6	−5.075	1.000	6.08	2.731
278	755	−35.9	−5.078	0 768	5.85	2.136
283	573	−37.1	−5.064	0 553	5.62	1.564
288	384	−38.4	−5.061	0.352	5.41	1.012
293	189	−39.7	−5.055	0.164	5.22	0.481
298	−13	−41.0	−5.059	−0 011	5.05	−0.032
303	−221	−42 3	−5 037	−0 174	4 86	−0.526
308	−436	−43.6	−5 024	−0 328	4 70	−1 005
313	−657	−44.8	−4 999	−0 469	4 53	−1.466
318	−884	−46.1	−4 988	−0.601	4 39	−1.911
323	−1118	−47 4	−4 967	−0 725	4 24	−2.343
328	−1358	−48.7	−4 949	−0 841	4.11	−2 760
333	−1605	−50.0	−4 929	−0 950	3 98	−3.165
			Sulfuric acid (second hydrogen)			
273	−146	−76 0	−11.148	−0.157	10.99	−0.428
278	−533	−78.9	−11.161	−0 542	10.62	−1.508
283	−934	−81 8	−11.165	−0.901	10 26	−2.550
288	−1351	−84 8	−11 177	−1.237	9.94	−3 561
293	−1782	−87.9	−11.173	−1 514	9 68	−4 435
298	−2229	−90 9†	−11 216	−1.842	9 38	−5 501
303	−2692	−94.1	−11.205	−2 165	9 04	−6.411
308	−3172	−97.3	−11 213	−2 374	8 84	−7 311
313	−3665	−100 6	−11 226	−2 613	8 60	−8.179
318	−4176	−103.7	−11 210	−2.833	8 38	−9 029
323	−4704	−107 2	−11.233	−3 052	8.18	−9.858
328	−5249	−110.7	−11 249	−3.255	8.00	−10.668
333	−5811	−114.1	−11 249	−3 441	7.81	−11 458
			dl-Alanine (K_A)‡			
293	913	−39.8	−5.068	0 794	5 86	2 325
298	720	−37.5	−4 627	0 595	5 22	1 777
303	538	−35.1	−4 180	0.423	4 60	1.281
308	369	−32 3	−3.722	0 276	4 00	0.851
313	215	−29.0	−3 236	0 153	3.39	0 480
318	79	−25 4	−2 746	0.054	2 80	0 171

† A mistake in ΔC_p was observed in the original data.

‡ ΔC_p was calculated by approximate methods from ΔH.

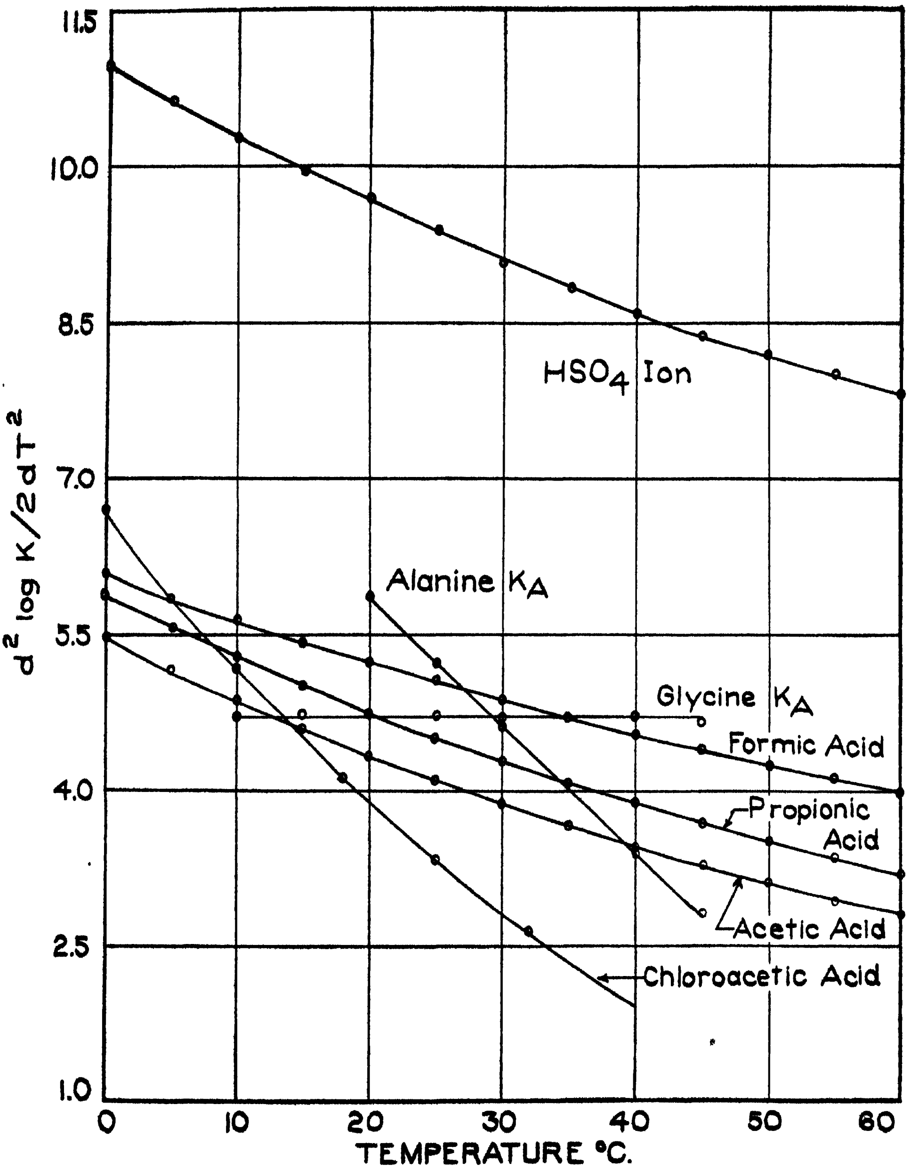

FIG. 1. VARIATION OF SECOND DERIVATIVE OF IONIZATION CONSTANT WITH TEMPERATURE

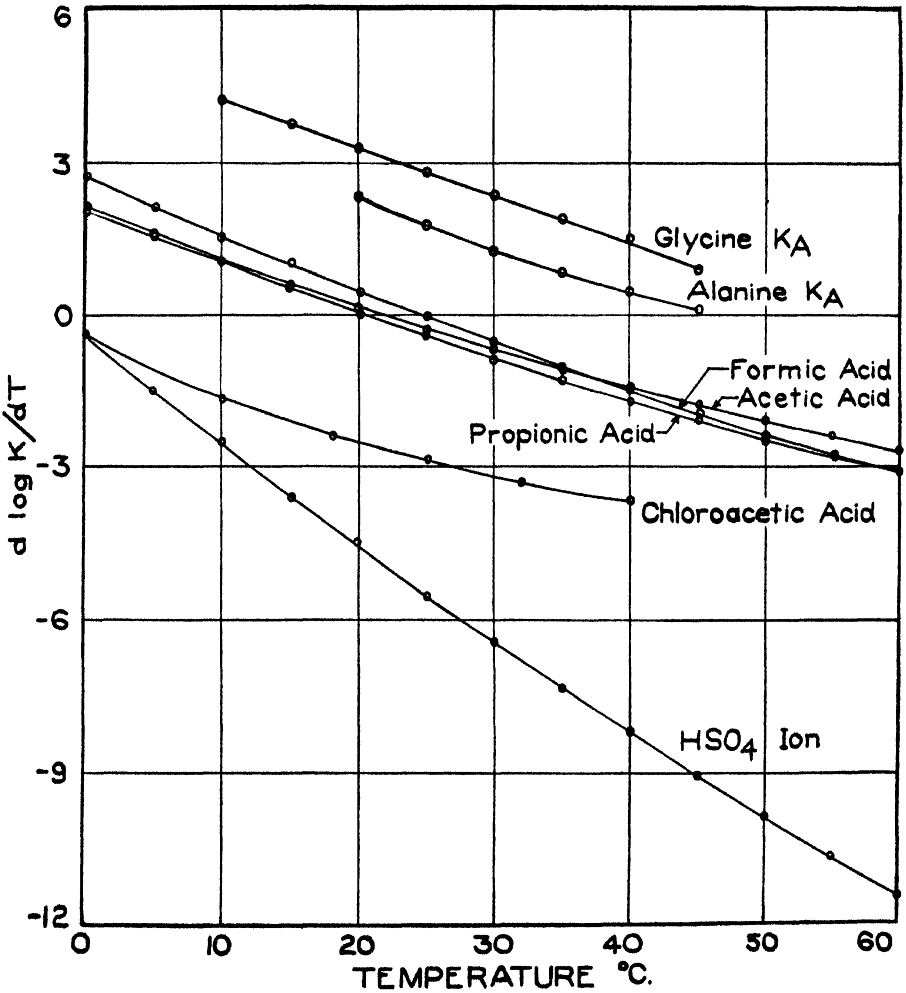

FIG. 2. VARIATION OF FIRST DERIVATIVE OF IONIZATION CONSTANT WITH TEMPERATURE

A tangent to any point on a curve in figure 1 then represents $\frac{\frac{1}{2}\mathrm{d}^3 \log K}{\mathrm{d}T^3}$, which can be determined by differentiating equation 13:

$$\frac{\mathrm{d}^3 \log K}{\mathrm{d}T^3} = \frac{-4\Delta C_p}{2.303RT^3} + \frac{6\Delta H}{2.303RT^4} + \frac{1}{2.303RT^2}\frac{\mathrm{d}(\Delta C_p)}{\mathrm{d}T} \tag{19}$$

This equation likewise expresses the rate at which $\Delta H/T$ is approaching ΔC_p.

Another method of testing whether or not log K is a quadratic function of temperature is to plot $\frac{\mathrm{d} \log K}{\mathrm{d}T}$ against temperature. Straight lines having the same slope should be obtained. The expression d log $K/\mathrm{d}T$ may be obtained by combining equations 8 and 9:

$$\frac{\Delta H}{2.303RT^2} = -2p(T - \theta_1) = \frac{\mathrm{d} \log K}{\mathrm{d}T} \tag{20}$$

The data for $\frac{\Delta H}{2.303RT^2}$ obtained in table 2 have been plotted in figure 2; the values do not fall on straight lines, showing that d log $K/\mathrm{d}T$ is not a linear function of temperature. The slopes of the lines are not the same for all acids.

Glycine is found to plot as a straight line. This fact must be true, however, since examination of the original article (8) shows that ΔH and ΔC_p apparently had been calculated under the assumption that log K was a quadratic function of temperature.

CONCLUSION

1. Log K is not a quadratic function of the temperature.
2. The theoretical significance of p and its relation to d log $K/\mathrm{d}T$ and d^2 log $K/\mathrm{d}T^2$ have been pointed out.
3. The significance of the third derivative has been pointed out for the first time.

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POTENTIALS OF CELLS INVOLVING MOVING BOUNDARIES[1]

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The thermodynamic treatment of a cell involving a liquid junction between two electrolytes having a common ion would be greatly simplified if the boundary between the two solutions could be regarded as a moving boundary such as is used in the determination of transference numbers (7), for under these conditions the potential of the cell becomes a simple function of the activity of the water in the two different solutions.

Referring to figure 1, consider, for example, the case of a cell involving a moving boundary, O_1–O_2, between solution I, C_1 normal with respect to lithium chloride, and solution II, C_2 normal with respect to potassium chloride. Using electrodes reversible to chloride ions, let 1 faraday of negative electricity pass through the cell from right to left, causing the boundary to sweep through V liters of solution to the new position O_3–O_4. Letting T_{Li} and T_{K} be the transference numbers of the cations in solutions I and II, respectively, it is apparent that T_{Li} equivalents of lithium cross O_1–O_2 into V, while T_{K} equivalents of potassium cross O_3–O_4 out of V. If it is assumed that the boundary is to be maintained without mixing the two solutions or changing their concentrations, the following relations must hold:

$$T_{\mathrm{Li}} = VC_1 \tag{1}$$

$$T_{\mathrm{K}} = VC_2 \tag{2}$$

On dividing equation 1 by equation 2 there results the familiar "regulating" equation, first derived in a more general form by Kohlrausch (3):

$$\frac{T_{\mathrm{Li}}}{T_{\mathrm{K}}} = \frac{C_1}{C_2} \tag{3}$$

When C_1 and C_2 are chosen so as to satisfy the above equations, the net transfer of chloride ion can be calculated as follows:

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[1] This article is based upon a thesis submitted by F. D. Martin to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

PROCESS	GAIN OR LOSS IN EQUIVALENTS PER FARADAY	
	Solution I	Solution II
Electrode reactions	Loses one equivalent	Gains one equivalent
Movement of the boundary	Gains VC_2 equivalents	Loses VC_2 equivalents
Transference across O_3–O_4	Gains $(1 - T_K)$ equivalents	Loses $(1 - T_K)$ equivalents
Net effect	Gains $VC_2 + (1 - T_K) - 1 = 0$	Loses $VC_2 + (1 - T_K) - 1 = 0$
	(For by equation 2, $VC_2 = T_K$)	

Since the concentrations are adjusted so that no mixing or transfer of the cations will occur, there is no net transfer of any of the three ions.

The transfer of water remains to be considered. It has been shown by MacInnes and Dole (6) that transference numbers calculated from experiments with moving boundaries are identical with Hittorf transference numbers, hence the transfer of water by the ions themselves need not be taken into account. There is, however, a transfer of water from solution II to solution I as a result of the movement of the boundary; the water originally present in V liters of II becomes a part of I as the boundary moves from O_1–O_2 to O_3–O_4. Let M_w be the number of moles of water thus transferred, and let a_1 and a_2 be the activities of the water in solutions I and II, respectively. The free energy change, ΔF, of the transfer will be:

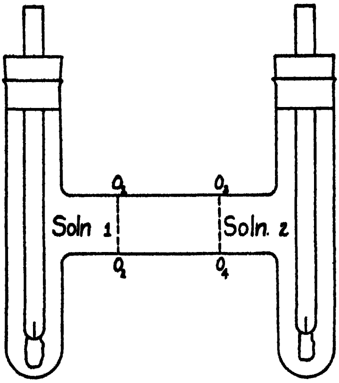

FIG. 1

$$\Delta F = M_w RT \ln \frac{a_1}{a_2} \tag{4}$$

Taking T as 298°K. and noting that M_w represents the number of moles transferred per faraday, the potential, E, of the cell represented in figure 1 becomes

$$E = 0.05915\, M_w \log_{10} \frac{a_2}{a_1} \tag{5}$$

Equation 5 provides a means for calculating the exact potential of such a cell, using data which is readily available. It is valid, however, only in case the passage of electricity through the cell brings about the movement of the boundary. Dole (1) has derived an equation similar to equation 5 to account for the deviations of the glass electrode in acid and in non-aqueous solutions.

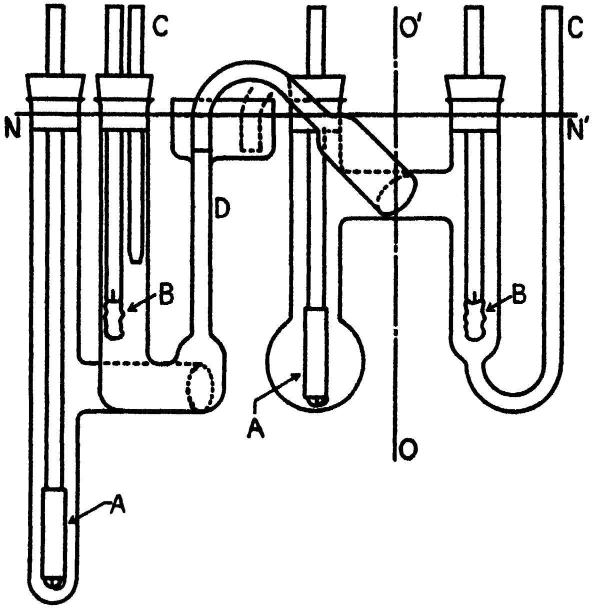

FIG. 2

EXPERIMENTAL

In an effort to test equation 5, a modification of the moving boundary apparatus developed by Brighton (4) was set up. As shown in figure 2, in addition to the compartments AA, containing the working electrodes for carrying the current used to establish the moving boundary, the compartments BB, were added, containing the potential electrodes for measuring the potential of the cell. The tubes CC furnished a means for renewing the electrolyte around the potential electrodes and for adjusting the surfaces of the two solutions before establishing contact. The boundaries were of the descending type and were made visible by an illuminated screen with a black horizon as recommended by MacInnes and Smith (8).

Thermostat. All runs were made in an oil thermostat at a temperature of 25.0°C.

Potentiometer and electrical system. A diagram of the electrical connections is shown in figure 3. The current used to establish the boundary could be regulated by the rheostats to any desired value, as read on the milliammeter, A. When a reading of the potential of the cell was being taken this current was shut off by switch S_1, while contact with the potential electrodes was established by means of switch S_2. A Leeds and Northrup Type K potentiometer was used.

Electrodes and solutions. Both the working and the potential electrodes were of the silver–silver chloride type. The former were made by silver plating cylindrical electrodes of platinum foil, then chloridizing the electrode which was to serve as cathode. The electrodes used for measuring the potential were made by filling platinum spirals, about 1 cm. long, with a paste of pure silver oxide, decomposing the oxide in an electric furnace, then chloridizing the resulting spongy silver in a dilute solution of hydrochloric acid for one to two hours. The electrodes were then thoroughly washed and stored in the solution in which they were to be used. Solutions of the chlorides of sodium, potassium, and lithium were used, solutions of the first two being prepared by direct weighing of the dry, recrystallized salts into calibrated volumetric flasks, while the lithium chloride solutions were prepared by weighing out the calculated amount of one of three different stock solutions, then diluting as before.

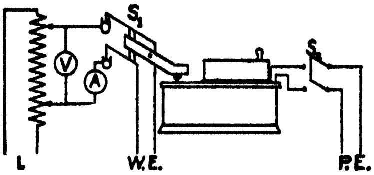

FIG. 3. ELECTRICAL CIRCUIT

L = 110 volts; W. E., to working electrodes; P. E., to potential electrodes

Procedure. In the first series of experiments, readings of the potential were taken about one second after the interruption of the current used to establish the boundary. Several different combinations of the three chlorides were used, the concentrations in each case conforming to the requirements of equation 3, as calculated from data in the International Critical Tables. Table 1 gives the results of this series of measurements, as compared with the values calculated from equation 5.

In view of the discrepancy between the observed and the predicted values of the potentials, the first series of runs was discontinued and a search begun for possible causes of the lack of agreement. The results of this investigation may be summarized as follows:

1. There appeared to be no serious error in the data used for calculating the potentials according to equation 5. The ratios of a_2/a_1 were calculated

from the vapor pressure lowerings of the various solutions as recorded in the International Critical Tables. Each value of M_w was calculated by three different methods with concordant results.

2. The experimental error was insufficient to account for differences amounting to several millivolts.

3. There remained to be considered the behavior of the boundary after the working current had been interrupted. In the derivation of equation 5 it was assumed that the boundary was maintained during the measurement of the potential of the cell. The experiments of MacInnes and Cowperthwaite (5) showed that the boundary faded slowly when the current was shut off and regained its original sharpness shortly after the current was turned on again. These observations were repeated and confirmed in this laboratory. In order to study further the effect of the interruption of the working current upon the potential of the cell, a second series of measurements was undertaken. In this series the working current was shut off after the boundary had been established, then readings of the potential were taken at short intervals until no further significant change was noted. The influence of other factors, such as the potential drop used to form the boundary and the concentration of the indicator solution, was also studied.

TABLE 1

Potentials of cells with liquid junction established by a moving boundary

$T = 25°C.$

SOLUTION I	SOLUTION II	POTENTIAL DROP IN II	AVERAGE POTENTIAL OF CELL	POTENTIAL CALCULATED FROM EQUATION 5
		volts per cm.	*millivolts*	*millivolts*
0.594 N LiCl	1.00 N KCl	2.3–2.7	−17.9	−8 4
0 303 N LiCl	0.50 N KCl	2.6	−17 9	−8 4
0.064 N LiCl	0 10 N KCl	2.4–2 8	−18.1	−8 33
0.77 N NaCl	1 00 N KCl	2.7	−11 0	−4.9
0 40 N NaCl	0.50 N KCl	2.6–3.0	−10 5	−4 15
0.303 N LiCl	0.40 N NaCl	2.5–3.0	−7 1	−4.27

The sign on the potential corresponds to the flow of negative electricity through the cell from solution II to solution I.

As the result of nearly one hundred runs using various concentrations of lithium chloride solutions against 0.10 N solutions of potassium chloride and sodium chloride, also different concentrations of sodium chloride solutions against 0.10 N potassium chloride solution, the following conclusions were drawn:

1. The "instantaneous" potential of a cell involving a moving boundary, taken within a fraction of a second after the interruption of the current used to establish the boundary, is not a constant but varies with the potential gradient used to form the boundary. As shown in figure 4, an

increase in the potential gradient causes a rise in the observed "instantaneous" potential of the cell.

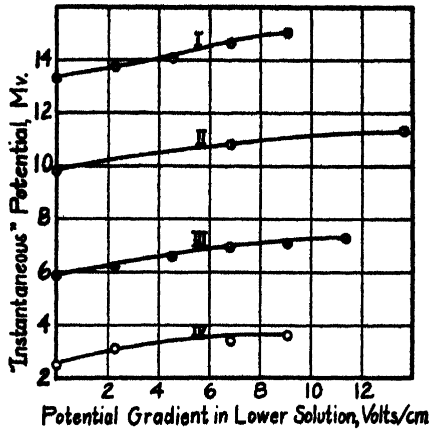

Fig. 4. Effect of Potential Gradient upon Instantaneous Potential

I, 0.1 *N* sodium chloride, using 0.050 *N* lithium chloride as indicator solution; II, 0.1 *N* sodium chloride, using 0.064 *N* lithium chloride as indicator solution; III, 0.1 *N* sodium chloride, using 0.0822 *N* lithium chloride as indicator solution; IV, 0.1 *N* sodium chloride, using 0.1000 *N* lithium chloride as indicator solution.

TABLE 2

Potential of the cell Ag, AgCl, 0.064 *N* LiCl, *junction formed by moving boundary,* 0.10 *N* KCl, AgCl, Ag

$T = 25°C.$

TIME INTERVAL BETWEEN INTERRUPTION OF CURRENT AND MEASUREMENT OF CELL POTENTIAL	POTENTIAL DROP IN KCl SOLUTION IN VOLTS PER CENTIMETER (5.7 MM. TUBE)			
	4.43	3.31	1.66	0.55
	Potential of the cell			
minutes	*mv.*	*mv.*	*mv.*	*mv.*
0.0	−17.9	−17.5	−17.1	−16.7
0.25	−16.5	−16.6	−16.6	−16.5
0.50	−16.5	−16.5	−16.6	−16.4
1.0	−16.4	−16.4	−16.6	−16.4
2.0	−16.4	−16.4	−16.5	−16.4
5.0	−16.4	−16.3	−16.4	−16.4
10.0	−16.4		−16.4	
15.0		−16.3		

Negative current flowed from right to left through the cell. Similar results were obtained for other pairs of solutions.

2. After the current used to form the boundary has been cut off, the potential of the cell diminishes with time, approaching a constant value. Although, as stated above, the instantaneous values of the potential of the

cell vary with potential gradient used to form the boundary, the final or equilibrium value, obtained after the lapse of several minutes, is constant and reproducible, depending only on the concentration and the composition of the solutions used. The data in table 2 furnish a typical illustration of this effect.

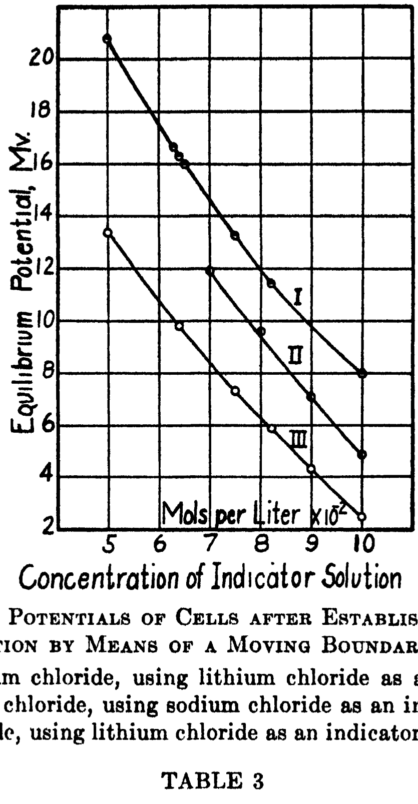

FIG. 5. EQUILIBRIUM POTENTIALS OF CELLS AFTER ESTABLISHING A LIQUID JUNCTION BY MEANS OF A MOVING BOUNDARY

I, 0.10 *N* potassium chloride, using lithium chloride as an indicator solution; II, 0.10 *N* potassium chloride, using sodium chloride as an indicator solution; III, 0.10 *N* sodium chloride, using lithium chloride as an indicator solution.

TABLE 3

Comparison of observed and calculated values of the liquid junction potentials

JUNCTION	LIQUID JUNCTION POTENTIAL	
	Observed by moving boundary method	Calculated from Lewis and Sargent formula
	mv.	*mv.*
0.1 *N* KCl, 0.1 *N* LiCl	8.0	7 4
0.1 *N* KCl, 0.1 *N* NaCl	4.88	4.9
0.1 *N* NaCl, 0.1 *N* LiCl	2.5	2.5

3. These equilibrium values of the potential vary in a regular manner with the concentration of the indicator solution. This is clearly shown in figure 5, where these equilibrium potentials are plotted against the concentrations of the various indicator solutions. Since there is no abrupt

change in the regions in which the concentrations of the indicator solutions are close to the "adjusted" values required by equation 3, there is no reason for believing that lack of agreement with equation 5 was due to any error in selecting an indicator solution of exactly the right concentration.

It may be of interest to point out that these equilibrium potentials for the 0.1 *N* solutions agree fairly well with the potentials calculated from the Lewis and Sargent formula (9). Table 3 gives a comparison of the observed and calculated values.

4. A possible explanation for the high potentials obtained experimentally, as compared with the values predicted from equation 5, may lie in a peculiar lag effect now being investigated in this laboratory. A preliminary report on this effect by Hunt and Chittum (2) showed that when a direct current is passed through an electrolyte and the fall in potential over a section of the solution measured by means of a set-up similar to that used for measuring the potentials in the present investigation, a distinct lag occurs when the current is interrupted, that is, the potential between the two electrodes dipping in the same solution does not instantly fall to zero when the current is shut off. Further investigation is necessary before deciding whether this lag effect will account for the observed deviations from the values predicted by equation 5.

SUMMARY

1. An equation has been derived for the potential of a cell involving a moving boundary between two electrolytes having a common ion.

2. Potentials of such cells were measured immediately after the interruption of the current used to establish the boundary. The experimental results were not in agreement with the equation.

3. Possible reasons for this disagreement were investigated without revealing the exact cause of the deviation. It is suggested that a lag effect now being studied in this laboratory may be involved.

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THERMOCHEMISTRY AND PHYSICAL PROPERTIES OF BROMIDES AND HYDROSULFIDES

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In a preceding paper (19) the size and symmetry of the SH^- ion was deduced from the crystal structures of the alkali hydrosulfides MeSH, where Me is Na, K, Rb, Cs, or NH_4. The union of a proton with the S^{--} ion may be considered to take place in either of two ways: first, the proton may enter the S^{--} nucleus with an energy change of the order of 10^6 volts to give a spherical Cl^- ion; second, it may penetrate only the outer electron shells and form an electron pair bond with the sulfur to give a SH^- dipole ion (internuclear distance, 1.4 A.U.; dipole moment, 0.65×10^{-18}), the energy change here being about 10 volts. In all three of these ions the outer electrons have configurations similar to that of argon. The ease with which the SH^- ion assumes effective spherical symmetry in crystals by rotation is evidence that the proton is quite deeply buried in the outer electron shells of the group and leads one to expect that SH^- will be more like a halogen than like the strongly polar OH^-. Because of the increase in radius over Cl^-, SH^- resembles more closely in size the next halogen Br^-, as the following list of crystal radii shows: I^-, 2.19; SH^-, 1.99; Br^-, 1.96; CN^-, 1.93; Cl^-, 1.81; F^-, 1.33. By reason of the similarity in the sizes and charges of their anions, ionic crystals of the type MeX where X is SH, Br, or CN will have similar Coulomb energies and consequently similar lattice energies. It is the purpose of this paper to present some thermochemical calculations based on these lattice energies, and further to extend the comparison of Br and SH compounds to a brief survey of the physical properties of their covalent compounds.

In calculations of the kind to be presented all errors are additive. While a complete elimination of minor inconsistencies in the large variety of data employed has not been attempted because of the considerable labor involved, the majority of derived values appear reliable to 5 kg-cal.; this accuracy is sufficient for the purposes in view. Heat evolved in a reaction is positively signed and is given in kilogram-calories per mole.

I. LATTICE ENERGY OF ALKALI COMPOUNDS MeX

The lattice energy of MeX, defined as the heat of the reaction

$$MeX_{crystal} \rightarrow Me^+ + X^- + (U)$$

may be calculated from the simple Born theory for ionic crystals. The calculations of Sherman (17) for MeBr and for MeCN are reproduced and his method is applied to MeSH. For sodium hydrosulfide, potassium hydrosulfide, and rubidium hydrosulfide the heat absorbed in raising the crystal from 25°C. to 200°C., which includes a heat of transition in addition to the usual specific heat terms, is neglected. For lithium hydrosulfide a hypothetical sodium chloride cubic phase is assumed whose cube edge is predicted from known radii; uncertain or estimated numerical quantities here as elsewhere are enclosed in parentheses (see table 1). Lattice energies for ammonium hydrosulfide and ammonium cyanide will be calculated by an indirect method in section IV.

From these lattice energies we may calculate the proton affinities of the anions, defined as the heat of the reaction

$$H^+ + X^- \rightarrow HX_g + (K)$$

by three independent processes, except in the case of SH^-, to which only two are applicable.

TABLE 1

Lattice energies of alkali compounds MeX

MeX	(a)MeSH	(n)MeSH	$-(U)$MeSH	$-(U)$MeBr	$-(U)$MeCN
LiX	(5.56)	7	(178)	183.1	
NaX	6.05	8	168	171.7	171
KX	6.63	9	155	157.8	156
RbX	6.93	10	150	152.5	150
CsX	4.29	11	143	143.5	142.5
NH_4X			149	147.4	148

II. CALCULATION OF PROTON AFFINITIES BY PROCESS I

This makes use of the cycle

$$\begin{tikzcd}
\text{Me} + \text{HX} \arrow[rr, "(W)"] & & \text{MeX} + 1/2\text{H}_2 \arrow[dl, "(U)"', "(I+D)\text{H}"] \\
& \text{Me}^+ + \text{X}^- + \text{H}^+ \arrow[ul, "(K)\text{X}^-"', "(I+S)\text{Me}"] &
\end{tikzcd}$$

The heat of reaction (W) is found by the equation

$$(W) = (Q)\text{MeX} - (Q)\text{HX}$$

the symbol (Q) denoting here as elsewhere the heat of formation from the elements; numerical values of this quantity are taken from Landolt-Börnstein, tables 320 and 321, except as noted. The constants $(I)\text{H} = 312$, $(D)\text{H} = 52$ will be used frequently in the following (see table 2).

III. CALCULATION OF PROTON AFFINITIES BY PROCESS II

This process makes use of the heat of solution of the gas ion $(L)X^-$. While this quantity could be calculated from the known radii by the method of Bernal and Fowler (1), a more reliable method combines the lattice energy (U)MeX, the heat of solution (L)MeX, and the heat of solution of the cation $(L)Me^+$; for the latter is used the "experimental" value of the same writers as shown in table 3, giving the average values for $(L)X^-$: SH^-, 60; CN^-, 58; Br^-, 58. This calculation neglects hydrolytic effects, which may introduce some uncertainty in the case of the cyanides. Using these values and the known heats of solution of H^+ and of HX, and the heat of dissociation of the weak acids, hydrosulfuric and hydrocyanic (dissociation constants 10^{-7} and 10^{-9}, respectively), we find the results given in table 4, in satisfactory agreement with the results of process I.

TABLE 2

Proton affinities by process I

	NaSH	KSH	NaCN	KCN	NaBr	KBr
(U)	−168	−155	−171	−156	−172	−158
(W)	51	58	52	62	78	86
$-(I + D)H$	−364	−364	−364	−364	−364	−364
$(I + S)Me$	144	121	144	121	+144	+121
$(K)X^-$	337	340	339	337	314	315

TABLE 3

Heats of hydration

	NaSH	KSH	NaCN	KCN	NaBr	KBr
U	−168	−155	−171	−156	−172	−158
$-(L)MeX$	−4	−1	0	3	0	+5
$(L)Me^+$	114	94	114	94	114	94
$(L)X^-$	58	62	57	59	58	59

TABLE 4

Proton affinities by process II

	HBr	HSH	HCN
$H^+ \rightarrow H^+_{aq}$	276	276	276
$X^- \rightarrow X^-_{aq}$	58	60	58
$H^+_{aq} + X^-_{aq} \rightarrow HX_{aq}$	$>-20<$	6	11
$HX_{aq} \rightarrow HX_g$		−5	−6
$H^+ + X^- \rightarrow HX_g + (K)$	314	337	339

Conversely this calculation shows convincingly that the weakness of hydrosulfuric and hydrocyanic acids in aqueous solution is a consequence of the relatively large proton affinity of the anion.

In the case of Br^- and CN^- the lattice energy (U)MeX yields a value for the electron affinity (E)X, or rather of the sum $(E + D)$X, where (D)X is the heat of dissociation of $1/2X_2$ into atoms. From this value of (E)X independent values for $(K)X^-$ are then easily found, in agreement with the foregoing values (see tables 5 and 6), or (E)Br = 85, $(E)CN^1$ = 69.

The agreement between (K) values calculated by the foregoing three methods points to a consistency in the experimental reaction heats employed, and suggests that the only uncertainty lies in the theoretical lattice energies. We therefore select the following (K) values: Br^-, 314; SH^-, 338; CN^-, 338. This readily gives (E)SH = 61, and permits the conclusion that while the covalent bond strengths H:Br and H:SH are equal, the proton affinities and electron affinities of the negative groups differ by 24 kg-cal.

TABLE 5

Electron affinities

	NaBr	KBr	NaCN	KCN
$(D + E)$*	59	58	32	29
(D)†	27	27	38.5	38.5
(E)	86	85	70.5	67.5

* Values from Sherman (17).

† Values of $(D)(CN)_2$ and (D)HCN from Kistiakowsky and Gershinowitz (J. Chem. Physics 1, 432 (1933)).

TABLE 6

Proton affinities by process III

	HSH	HBr	HCN
(D)HX*	87	87	94.5
(I)H	312	312	312
(E)X		−85	−69
$(K)X^-$		314	337.5

* See second footnote to table 5.

Taken in conjunction with the lattice energies of section I, they also permit the calculation of the following heats of formation: lithium hydrosulfide (hypothetical), (47); rubidium hydrosulfide, (65); cesium hydrosulfide, (65); and of the lattice energy of NH_4X as follows.

---

[1] Lederle (Z. physik. Chem. 17B, 361 (1932)) gives $(E)(CN)$ = 92 ± 2.

IV. LATTICE ENERGY OF NH_4X

The proton affinity of NH_3

$$NH_3 + H^+ \rightarrow NH_4^+ + (P)$$

enters into the following cycle:

$$\begin{tikzcd}
NH_{3\,gas} + HX_g \arrow[rr, "W'"] & & NH_4X_{crystal} \arrow[dl, "U"] \\
& NH_4^+ + X^- \arrow[ul, "(K)", "-(P)"'] &
\end{tikzcd}$$

TABLE 7

Lattice energies of ammonium salts

	NH_4Br	NH_4SH	NH_4CN
(W')	45.0	22.4	20.6
(K)	314	338	338
$-(P)$	−211	−211	−211
(U)	148	149	148

TABLE 8

Lattice energies of ammonium salts

	NH_4Br	NH_4SH
$(L)NH_4X$	−4	−3
$(L)NH_4^+$	−87	−87
$(L)X^-$	−58	−60
$(U)NH_4X$	−149	−150

From W' (Landolt-Börnstein), $(K)HX$ (given in section III), and $(U)NH_4X$ (Sherman) are calculated the following values of (P): ammonium chloride, 214; ammonium bromide, 213; ammonium iodide, 206; or $P_{av.} = 211$. This differs immaterially from Sherman's value for the same constant. From the same cycle are now calculated the lattice energies of ammonium hydrosulfide, which has the PH_4I structure for which the Madelung constant has not yet been given, and of ammonium cyanide whose crystal structure has not been reported (see table 7). This shows that, as in the case of the alkali metals, the three ammonium salts have identical lattice energies and therefore that ammonium hydrosulfide and ammonium cyanide are presumably ionic crystals.

The same value of $(U)NH_4SH$ may be calculated from its reported heat of solution (see table 8).

V. THE STABILITY OF MeSH UNDER VARIOUS CONDITIONS

The ability of lithium hydrosulfide to exist in a stable anhydrous solid form is at least questionable. We are in a position to make an estimate of its stability with respect to the decomposition

$$Li_2S + H_2S \rightarrow 2LiSH + \Delta H$$

and to compare it with the other alkali hydrosulfides.

TABLE 9

Heat of formation of lithium hydrosulfide

(Q)LiSH	(47)
(U)LiSH	−(178)
$(L)Li^+$	136
$(L)SH^-$	60
$(Q)LiSH_{aq}$	(65) calculated
$(Q)LiSH_{aq}$	70 observed

TABLE 10

Dissociation of solid alkali hydrosulfides

	Li	Na	K	Rb
$-(Q)Me_2S$	−(111)*	−89	−87	−87
$-(Q)H_2S$	−5	−5	−5	−5
$2(Q)$MeSH	(94)	113	126	(130)
(ΔH)	−(22)	19	34	38
$(T\Delta S)$†	−(11)	−(11)	−(11)	−(11)
(ΔF)	−(33)	(8)	(23)	(27)

* $(Q)Li_2S$ is assumed equal to (Q)SrS; see Guntz and Benoit (Ann. chim. **20**, 5 (1923)).

† The entropy change is a rough estimate and is assumed independent of the alkali metal involved.

In section I it was assumed that if lithium hydrosulfide existed it would have a sodium chloride cubic structure; thus the cube edge, lattice energy, and heat of formation were readily predicted from known radii of crystal ions. These calculated quantities are seen to be consistent when we deduce from them a value for the heat of formation of aqueous lithium hydrosulfide and compare it with the experimental value given in Landolt-Börnstein (see table 9).

The heat and free energy changes of the foregoing decomposition of MeSH, including hypothetical lithium hydrosulfide, are now calculated from heats of formation as given in table 10.

The calculated free energy changes indicate that MeSH is increasingly stable as the atomic number of the cation increases. This is in agreement with the qualitative observations of other writers on the stability of sodium hydrosulfide and potassium hydrosulfide. The negative value of the free energy change for lithium hydrosulfide shows that this hypothetical phase is thermodynamically unstable at ordinary temperatures. Similar deductions could be made from an application of the Nernst approximation formula.

It seems probable that the anhydrous hydrosulfides of the divalent metals—magnesium, calcium, strontium, barium, etc.—will be similarly unstable with respect to this decomposition. An experimental attack on this problem, which apparently has not been tried, would be the determination of equilibrium pressures of hydrogen sulfide over the solid phases MeSH–Me_2S, etc. On the contrary, it is easily shown from known heats of formation that the hydroxides of all the alkali and alkaline earth metals are thermodynamically stable with respect to the corresponding decomposition into water and the metal oxide.

The stability of MeSH in the presence of an alkali metal is also of some interest. When the hydrogens of hydrogen sulfide are successively replaced by Me in the two steps

$$\mathrm{Me} + \mathrm{H{-}SH} \rightarrow \mathrm{MeSH} + 1/2\mathrm{H_2} + (W)$$

and

$$\mathrm{Me} + \mathrm{MeSH} \rightarrow \mathrm{Me_2S} + 1/2\mathrm{H_2} + (Z)$$

each step evolves considerable heat. This is in accord with the observation that the alkali hydrosulfides are readily decomposed by alkali metals. In contrast to this it is known that the molten hydroxides of sodium and potassium are not only stable in contact with the metal but appear to take up a quantity of the metal in true solution (8); this agrees with the calculated negative heats of reaction, Z, for these hydroxides.

Numerical values of the foregoing reaction heats, including that of the reaction

$$2\mathrm{Me} + \mathrm{H_2S} \rightarrow \mathrm{Me_2S} + \mathrm{H_2} + (Y)$$

are tabulated in table 11.

VI. LATTICE ENERGIES OF ALKALI SULFIDES AND DERIVED CONSTANTS

The lattice energies of the alkali sulfides are now calculated by the Born method (see table 12). Sherman's value for sodium sulfide is reproduced; the cube edge of rubidium sulfide is derived from the reported density 2.912.

$$\begin{tikzcd}
2Me + H_2S \arrow[r, "Y"] & Me_2S + H_2 \arrow[d, "U"', "2(I+D)H"] \\
& 2Me^+ + S^{--} + 2H^+ \arrow[ul, "2(I+S)Me"', "L"]
\end{tikzcd}$$

The quantities

$$S^{--} + 2H^+ \rightarrow H_2S + (L)$$
$$S^{--} \rightarrow S + 2e + (E')$$

are derived by simple cycles from the lattice energies (U'). They do not differ seriously from values which may be calculated from Sherman's lattice energies of the alkaline earth sulfides.

TABLE 11

Decomposition of alkali hydrosulfides

	Li	Na	K	Rb
$(Q)Me_2S$	(111)	89	87	87
$-(Q)H_2S$	−5	−5	−5	−5
Y	(106)	84	82	82
W	(42)	51	58	(60)
Z	(64)	33	24	(22)

TABLE 12

Lattice energies of alkali sulfides

	a	n	$-U'$	L
Li_2S	5.70	7	576	(872)
Na_2S	6.53	8	516	869
K_2S	7.35	9	465	866
Rb_2S	(7.71)	9.5	(446)	(858)
				868

From the adopted values $(K) = 338$, $(L) = 868$, are found further the reaction heats[2]

$$S^{--} + H^+ \rightarrow SH^- + (H):\ H = L - K = 530$$
$$S^{--} + H_2S \rightarrow 2SH^- + (M):\ M = L - 2K = 192$$

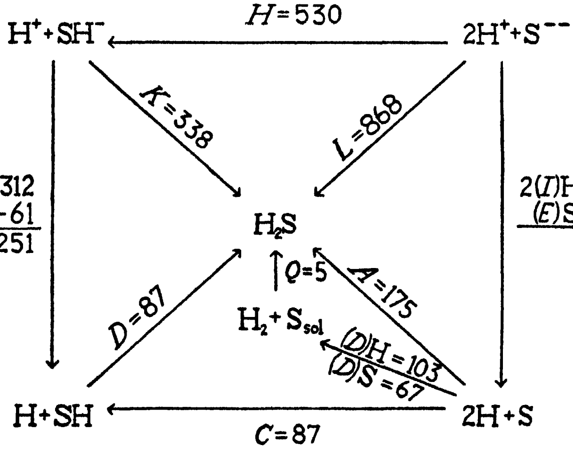
The thermochemical constants for hydrogen sulfide are summarized in diagram 1.

---

[2] Approximate values for H, K, L have been deduced by Hund (Z. Physik **32**, 1 (1925)) from a model for the hydrogen sulfide molecule.

Finally the heat of hydrolysis of the S^{--} gas ion may be calculated by either of two cycles, as given in tables 13 and 14.

$$S_g^{--} + H_2O_{liq} \rightarrow SH_{aq}^- + OH_{aq}^- + (J)$$



Heat cycles for H_2S molecule

DIAGRAM 1

TABLE 13

Calculation of the heat of hydrolysis of the S^{--} gas ion

	Li_2S	Na_2S	K_2S	Rb_2S
U	−576	−516	−465	−(446)†
$-(L)Me_2S$	−(11)*	−16	−23	−25
$2(L)Me^+$	272	228	188	174
J	(315)	304	300	(297)

* From $(Q)Li_2S_{aq} - (Q)Li_2S = 122 - (111) = (11)$.

† Lattice energy calculated from reported density.

TABLE 14

Calculation of the heat of hydrolysis of the S^{--} gas ion

$H^+ \rightarrow H_{aq}^+$	276	$HOH_{liq} \rightarrow HOH_g$	−10
$OH^- \rightarrow OH_{aq}^-$	$(L)OH^-$	$HOH_g \rightarrow H^+ + OH^-$	$-(280 + (L)OH^-)$
$H_{aq}^+ + OH_{aq}^- \rightarrow HOH_{aq}$	14	$S^{--} + H^+ \rightarrow SH^-$	530
$HOH_{aq} \rightarrow HOH_g$	−10	$SH^- \rightarrow SH_{aq}^-$	60
		$OH^- \rightarrow OH_{aq}^-$	$+(L)OH$
$(K)OH^-$*	$280 + (L)OH^-$	(J)	300

* Precisely this same value, $(K)OH^- = 280 + (L)OH^-$, follows from the experimental heats of reaction of the alkali metals with water when combined with the ionic heats of hydration used above.

If instead of the alkali sulfides the alkaline earth sulfides are used as a basis of calculation, somewhat larger values of (J) are obtained, similar to the case of the quantities (L), (H), etc., already mentioned.

The second method (table 14) introduces the proton affinity $(K)\mathrm{OH}^-$.

The two methods thus give identical results, namely $(J)\mathrm{S}^{--} = 300$, or a somewhat greater value from the alkaline earth sulfides.

VII. THE PROTON AFFINITY OF OH^- AND OF SeH^-

The proton affinity $(K)\mathrm{OH}^-$ may be calculated in terms of $(U)\mathrm{NaOH}$ or of $(L)\mathrm{OH}^-$ by the methods outlined in preceding paragraphs. Thus

$$(K)\mathrm{OH}^- = 175 - (U)\mathrm{NaOH};\ (L)\mathrm{OH}^- = -104 - (U)\mathrm{NaOH}$$

Previously proposed values for these constants are as follows:

$$\begin{array}{lll} & (K)\mathrm{OH}^- = 370 \pm 30 & \text{Hund from model (10)} \\ (U)\mathrm{NaOH} = 186 \pm 5, & (K)\mathrm{OH}^- = 360 \pm 5 & \text{Garrick (5)} \\ (L)\mathrm{OH}^- = 105, & (K)\mathrm{OH}^- = 385 & \text{Bernal (1) from radius OH}^- \end{array}$$

From x-ray powder data at 300°C. I have some evidence that the high temperature modification of sodium hydroxide has the sodium chloride structure with $a = 5.00$; from this may be calculated the radius of $\mathrm{OH}^- = 1.50$, the lattice energy $(U)\mathrm{NaOH} = 201$ kg-cal., and $(L)\mathrm{OH}^- = 97$. This gives a fourth value, namely $(K)\mathrm{OH}^- = 376$. We take the average of the four values, none of which appears very reliable, as $(K)\mathrm{OH}^- = 373 \pm 20$.[3] From this and the heat of dissociation, $(D)\mathrm{HOH} = 115$, may be calculated the electron affinity of OH as $(E)\mathrm{OH} = 54 \pm 20$.[4]

It is also possible to estimate the proton affinity of SeH^-. By process II, given

$$\mathrm{H_2Se_g} \rightarrow \mathrm{H^+_{aq}} + \mathrm{SeH^-_{aq}} + 3\ (\pm 10)$$

and assuming $(L)\mathrm{SeH}^- = 55 \pm 10$, we find $(K)\mathrm{SeH}^- = 328 \pm 20$. Further, given $(W')\mathrm{NH_4SeH} = 30$ and assuming $(U)\mathrm{NH_4SeH} = -146 \pm 10$ we find $(K)\mathrm{SeH}^- = 327 \pm 10$.

Thus 328 ± 20 seems a safe estimate for this quantity, and from it and the known heat of dissociation, $(D)\mathrm{H} - \mathrm{SeH} = 67$, may be found such further constants as may be desired.

The constants proposed above for SH, CN, OH, and SeH are now tabulated (table 15) for comparison with accepted values for some other univalent anions. These constants are related by the equation

$$(K) - (I)\mathrm{H} = (D) + (E)$$

where $(I)\mathrm{H} = 312$.

---

[3] H. Smyth and D. Miller (Phys. Rev. 43, 116 (1933)) recently found $(K)\mathrm{OH}^- = 460 \pm 115$.

[4] E. Lederle (Z. physik. Chem. 17B, 368 (1932)) gives $(E)\mathrm{OH} = 88 \pm 1$.

VIII. COVALENT BOND ENERGIES

It has already been pointed out that the S:H and Br:H covalent bond energies are both equal to 87 kg-cal. Likewise it has been shown (15, 16) that the S:C and Br:C covalent bond energies are both about equal to 67 kg-cal. The consequence of these coincidences is that the thermochemistry of organic bromides and mercaptans will be largely similar. This statement may be verified for such simple reactions as

$$>C{=}C< + HX \rightarrow >CH{-}CX<$$
$$ROH + HX \rightarrow RX + H_2O$$

where X is Br or SH, by the use of the compilation of Parks and Huffman (14).

TABLE 15

Comparison of gas ions and their hydrides

X	$(K)X^-$	$-(E)X$	$(D)HX$	$(L)X^-$	CRYSTAL RADIUS X^-	DISTANCE H − X
I	307	76	71	47	2 19	1 616
Br	314	85	87	58	1 96	1 420
SeH	(328)	(51)	67	(55)		
SH	338	61	87	60	1 99	1 43
CN	338	68 5	94 5	58	1 93	
Cl	326	88	102	65	1 81	1 282
F	361	98 5	148	97	1 33	0 923
OH	(373)	(54)	115	(93)		0 96
H	400	16	103			0 75

According to these figures the difference $(K - L)X^-$ is equal to 260 for the four strong hydrogen halide acids, while for the weak acids HSH, HCN, and HOH it is 20 kg-cal. greater, or 280.

According to this analysis the reactions

$$MeSH_s + HBr_g \rightarrow MeBr_s + HSH_g + \Delta H_1$$
$$MeSH_s + RBr_g \rightarrow MeBr_s + RSH_g + \Delta H_2$$

will have

$$\Delta H_1 = \Delta H_2 = (E)Br - (E)SH = 85 - 61 = 24 \text{ kg-cal.}$$

this statement is also easily verified. The second of these reactions is commonly employed in the preparation of the mercaptans, RSH; in view of the large heat change it is readily understood why they both run to completion. On the contrary the reaction

$$HBr + RSH \rightleftharpoons RBr + HSH$$

would have only a small heat change and therefore might be expected to give an equilibrium of reactants and products. It may also be shown that the reaction

$$HBr_g + MeCN_s \rightarrow HCN_g + MeBr_s + \Delta H$$

will have

$$\Delta H = (K)CN^- - (K)Br^- = 338 - 314 = 24 \text{ kg-cal.}$$

IX. SOME PHYSICAL PROPERTIES OF COVALENT BROMIDES AND HYDROSULFIDES

Familiar examples of comparable covalent compounds containing Br, SH, and CN radicals are the hydrides (HX), the dimers (XX),[5] and the carbon compounds (RX); of these the hydrides have been the most intensively studied. While it would be unwise to generalize from these to other covalent compounds, nevertheless the similarities in these three types are at least very suggestive. The molecules H:X and R:X, where X is Br or SH, are moderately polar, while the HCN and RCN molecules are strongly polar. The X—X molecules are symmetrical and non-polar. The hydrogen sulfide molecule is angular; hydrogen cyanide is linear.

In these compounds the space requirements of Br, SH, and CN are generally similar as calculated by the numerous methods available. For example, the additive parachors 68.0, 65.3, and 63.9, the additive mole volumes at the boiling point, 27.6, 29.4, and 30.5, respectively, have been proposed for the Br, SH, and CN groups. The mean free paths of hydrogen bromide and hydrogen sulfide at a given temperature, as calculated from gas viscosity data, differ by only 5 per cent, but that of hydrogen cyanide is considerably shorter. Similarly van der Waals' *b*, as calculated from critical constants, is nearly the same for hydrogen bromide and hydrogen sulfide, but is considerably larger for hydrogen cyanide.

Neither do the additive mole refractions of —Br and —SH differ greatly, however calculated; commonly used values are —Br, 8.87, and —SH, 8.79. This shows that the electrons are similarly bound in the two groups. Bromides and hydrosulfides thus have nearly the same refractive indices under the same conditions, as well as mole refractions. The considerably lower mole refraction of —CN, 5.54, is accounted for by supposing that the electron shells are more tightly bound in this group. Liquid H_2S_2 is distinguished from H_2O_2 in having normal values for its parachor and mole refraction; a rather large electric moment has been attributed to the hydrogen peroxide molecule.

The attractive forces between molecules, indicated by such constants as the heat of vaporization, van der Waals' *a*, the Sutherland constant *C*, the critical temperature, etc., are similar where known for corresponding bromides and hydrosulfides; but relative to these they are large for hydrogen cyanide and the nitriles and small for cyanogen. The analysis of these forces according to London's theory shows that while the dispersion effect predominates in hydrogen bromide (13) and hydrogen sulfide (2), the orientation effect is greatest in the hydrogen cyanide (2) molecule.

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[5] Physical properties of $(SH)_2$ are given by Butler and Maass (J. Am. Chem. Soc. 52, 2197 (1930)).

Finally the valence forces within the molecule have been shown to be similar for the H:Br and H:S and also for the C:Br and C:S linkages by calculation from their characteristic Raman frequency shifts (12).

It is of interest that cubic hydrogen sulfide and hydrogen bromide crystals form an uninterrupted series of solid solutions. The structure is a close packing of rotating molecules and is indistinguishable from that of the rare gases. On further cooling both crystals undergo transitions in which the dipole molecules become rigidly oriented, as shown by the sudden drop in the dielectric constant (9, 11, 18) and specific heat (3, 6) curves. Thus the parallelism in the physical properties of these two substances extends from the critical state down to the lowest temperatures at which they have been investigated. The properties of crystalline hydrogen cyanide have not been studied.

Ellis and Reid (4) have tabulated some physical constants of some liquid *n*-alkyl bromides and mercaptans, although they fail to stress the evident similarities. From the nonyl down through the amyl compounds and in some cases beyond, the following constants lie remarkably close together in the two series: melting point, normal boiling point, expansion coefficient mole volume, refraction, mole refraction. Bromides and mercaptans are normal unassociated liquids, nitriles are highly associated, as shown by fluidity and surface tension measurements. Although bromides and mercaptans differ in chemical properties, it is evident that they form a more logical pair for comparison of physical properties than mercaptans and alcohols as inevitably heretofore. That the SH radical would have this character of a halogen was implied by Grimm's hydride displacement rule (7).

The statements of this section are illustrated by the accompanying tabulations of physical constants (see table 16).

X. SUMMARY

Corresponding alkali bromides and hydrosulfides have nearly the same lattice energies; the proton affinities of Br^- and SH^- differ by about 23 kg-cal. The stability of the alkali hydrosulfides alone and in the presence of an alkali metal is treated from a thermochemical standpoint. Some reaction heats are deduced from the lattice energies of the alkali monosulfides. A brief survey of the physical properties of corresponding covalent bromides and hydrosulfides discloses some notable similarities. The foregoing treatment is extended in some cases to include cyanogen compounds.

TABLE 16

*Physical properties of covalent bromides, hydrosulfides, and cyanides**

	HBr	HSH	HCN	Br_2	$(SH)_2$	$(CN)_2$	EtBr	EtSH	EtCN
Dipole moment	0.79	0.93	2 65	0		(0 3)	1 86	(1.39)	3.4–3.7
Parachor (observed)	85.4	82 9	81.5	132.1	130.0		167.6	159.3	
Mole volume at boiling point (observed)	37.4	35.2	38.8	53.4	53.0	60 4		77.6	78.5
Mole refraction	9.15	9 64	6 48	17.44	17.73	12.32	19.11	19.19	15.78
Refractive index (liquid)	1.325	1.384	1 268	1 648	1.632		1.424	1.427	1.369
Refractive index (gas)†	0.573	0.642	0 438	1.132		0.850			
Melting point	−86	−83	−14	−7	−90	−28	−119	−147	−104
Boiling point	−68	−60	26	59	71	−20	38	35	98
Heat of vaporization	3.9–4.2	4.5–5.2	6.1–6.6	7.0	8.5	5.4–5.8	6.4–6.7	6.9	7.4
Critical temperature	90	100	184	301	(278)	127	236	228	291
Sutherland constant	375	331	901	460		330			
Entropy S_{298}	47.5	48 2	48 2	59.1		57.8			
Raman shift	2558	2615	3220				594	704	
Force constant, *f*	3.56	3.88					2.61	3.01	
Mass	80 92	34 08	27 02						
Outer electrons	36	18	14						
Nuclear charge of X	35	16 + 1	6 + 7						
Zero point volume	27.3	26.9							
Cube edge	5.78	5.77							
Relative mean free path‡	202 5	214.5	142.4						
Critical pressure	84	89	53						
Van der Waals' *a*	887	883	2220						
b	1978	1914	3920						

* From Landolt-Börnstein Tabellen, or recent sources.

† $(n_{\mathrm{D}} - 1)\ 10^3$.

‡ Gas viscosity at 20°C. divided by square root of molecular weight.

Dr. Linus Pauling first suggested to me that the thermochemistry of the hydrosulfides might be worth investigating from the point of view adopted in this paper. My best thanks go to Dr. H. M. Smallwood for his generous help in criticising the material here presented.

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THE EFFECT OF CATHODE RAYS ON HYDROPHOBIC SOLS

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The action of ionizing radiations on colloids was first investigated by Hardy (8) in 1903. He found that positively charged globulin sols were coagulated by β-rays from radium, while negatively charged sols were rendered more disperse. Henri and Meyer (9) reported that β-rays discharged the positively charged ferric hydroxide but not negatively charged sols. Fernau and Pauli (7) obtained coagulation of ceric hydroxide and albumin, by exposure to both β-rays and x-rays. Using x-rays Wels and Thiele (14) found that aggregate formation occurred in globulin sols on both sides of the isoelectric point, and hence was independent of the sign of the particle charge. Nordenson (12) studied the influence of ultraviolet light, x-rays, and β-rays on gold sols, and found that positively and negatively charged sols were coagulated at about the same rate. Crowther and Fairbrother (5) found that copper and iron sols which are positively charged were coagulated on exposure to large quantities of x-rays, and that silver and gold sols, which are negatively charged, were rendered more stable. Clark and Pickett (3) worked with positively charged colloidal lead and found it stabilized by exposure to x-rays. Lal and Ganguly (10) studied the coagulating influence of ultra-violet light and concluded that the stability of the sol was decreased, whether the sol was positively or negatively charged. In a recent paper, Boutaric and Roy (1) report that the γ-rays from radioactive materials do not affect colloid stability, and that the β-rays coagulate positively charged sols but do not affect the stability of negatively charged sols. They investigated sols of ferric hydroxide and gum mastic. Clark (2) states, "At present the results are still so conflicting due to large effects of impurities, sensitiveness to hydrogen-ion concentration, and other unknown eccentricities, such as internal photoelectric action, that no definite conclusions or rules can be established." (See also references 6 and 13.)

The present investigation was undertaken to obtain some definite information regarding the effect of ionizing radiations on colloids. Cathode rays were chosen for the experiments, (1) because of their simple nature and their high energy, (2) because the number of electrons emitted per second and the energy of the electrons could be varied independently, and (3) because, as far as could be ascertained, the effect of cathode rays on colloids had not previously been investigated.

The cathode-ray tube was of the simple form originally designed by Coolidge. It was operated by a transformer system similar to that described by him (4). The voltage applied to the tube was of the order of 150 kilovolts, and tube currents from 0.15 to 0.25 milliampere were used. The reaction cell was composed of two circular sheets of mica, 5 cm. in diameter and 0.0025 cm. thick, separated by a ring of glass 1.3 cm. thick. Washers were placed on the outer surface of each mica disc, and the combination was tightly clamped in a heavy brass container, by a screw counter cell. The liquid bombarded was thus only in contact with glass and mica, and the cell could easily be taken apart to be cleaned. The cell was connected to earth, and placed directly in front of the window and as close to it as possible.

In the first set of experiments the colloids were simply bombarded with the cathode rays and observed to see if coagulation had occurred. In the second set, samples not coagulated by bombardment were tested with electrolyte for change in stability. In the third set of experiments, the cataphoretic mobility of the sol particles was measured before bombardment, and after various lengths of exposure to the rays. Samples of sols not exposed to the rays, but otherwise subjected to the same manipulation as the treated samples, were used as controls. These controls gave no evidence of decrease in stability. The metallic sols were all made by the high frequency under water sparking method, but differed in concentration, even from sample to sample of sols of the same metal.

The results of the first two sets of experiments are shown in table 1. Two typical series of results of the third set are shown in table 2. Mobilities were measured one hour after the bombardment was completed. The gold sol used had a high conductivity, as it was stabilized with a small amount of potassium hydroxide; the copper sol had a low conductivity, as its dispersion medium was doubly distilled water. On bombardment the conductivity increased for sols of low initial conductivity, but it was not measurably affected when the initial conductivity of the sol was high.

No appreciable change in the conductivity of colloids or water took place on standing in the cell; moreover, no appreciable change in the conductivity of the water was observed due to exposure to cathode rays. This shows that decrease in stability cannot result from absorption of electrolytic impurities from the cell. Under bombardment the sol was never heated to a temperature higher than 40°C.; this rise in temperature does not account for the changes produced, for most of the sols could be boiled without coagulating.

The results thus indicate that the stability of both positively and negatively charged sols is decreased by exposure to cathode rays. This is in agreement with the theoretical considerations outlined below.

The cathode rays in passing through the sols will, on collision, give up their kinetic energy and their charge. The extra charge introduced by the cathode rays must eventually escape to earth, and can only affect the sol stability when adsorbed by the sol particles; in this case the stability will be increased or decreased according to whether the sol is negatively or positively charged. The kinetic energy given up by the cathode rays will result in the production of ionization. Ionization of the dispersion medium means an increase in the effective electrolyte concentration, which, in general, will bring about a decrease in sol stability irrespective of the

TABLE 1

The effect of cathode rays on the stability of sols

SOL	TUBE CURRENT	TUBE VOLTAGE	LENGTH OF EXPOSURE	RESULTS
	milli-amperes	*volts* × 10^3	*hours*	
Copper	0 12	140	5	Coagulated
	0 25	140	1 5	Coagulated
	0 21	150	1	Coagulated
	0.18	150	1.25	Coagulated
	0 25	160	2 5	Less stable to electrolytes
	0 25	160	1	Coagulated on standing
	0 25	160	1.5	Coagulated on standing
	0 25	160	0 5	Coagulated on standing
Gold	0 12	153	3 5	Not coagulated
	0 12	148	4	Not coagulated
	0.25	150	2	Electrolyte test not definite
	0 25	150	0 75	Less stable to electrolytes
		160	2	
	0 25	160	2	Less stable to electrolytes
	0 25	160	3	Coagulated on standing
Silver	0 25	150	2	Less stable to electrolytes
	0 25	160	2.5	Coagulated
	0 21	160	1 5	Coagulated on standing
Ferric hydroxide	0 25	127	1 25	Not coagulated
		150	2	
	0 21	150	2	Less stable to electrolytes
Lead	0.25	160	1.5	Coagulated on standing
Bismuth	0.25	160	1	Coagulated on standing
Platinum	0.25	160	2	Coagulated on standing
Arsenious sulfide	0 25	160	3 5	Very turbid, partially coagulated

sign of the charge of the sol particles. Unless some permanent chemical reaction results, the positive and negative ions will recombine and the net result will be the production of heat. On collision some of the energy will be used in the production of x-rays, but the percentage of energy so used will be small, for Clark states that even in an x-ray tube at least 98 per cent of the electron energy goes to the heating of the target. The total change in stability will thus depend on the ratio of the effect produced by the transfer of charge to the sol particles to that produced by the ionization of the medium. For a 0.1 per cent gold sol the ratio of the probability of collision of a cathode ray with a gold particle to the probability of collision with a water molecule is about 1:10^7, so that it seems quite reasonable that, in general, decrease of stability will result on exposure.

TABLE 2

The effect of cathode rays on the mobility of sol particles

Tube voltage, 160 kilovolts; current, 125 milliamperes

DURATION OF CATHODE RAY BOMBARDMENT	CONDUCTIVITY	MOBILITY
	Gold sol, 0.0262 g. per 100 cc.	
	ohms^{-1} *cm.*$^{-1}$	*cm. per second per volt per cm.*
Untreated	1.9×10^{-4}	0.00018
Control		0.00018
0 5 hour		0.00016
1.0 hour		0.00013
1 5 hours		0.00011
Untreated		0.00018
Control		0.00018
0.5 hour		0 00016
	Copper sol, 0.0128 g. per 100 cc.	
Untreated	7.9×10^{-6}	0.00020
Control	8.0×10^{-6}	0.00020
0.5 hour	11×10^{-6}	0.00015
1.0 hour	16×10^{-6}	0.00015
1.5 hour	17×10^{-6}	0.00012 (Coagulated after 3 hrs.)
Untreated	8.0×10^{-6}	0.00020
0 5 hour	12×10^{-6}	0.00015
1.0 hour	19×10^{-6}	0.00015 (Coagulated after 5 hrs.)
1.5 hours		

Lind (11) states, "The chemical effects of α- and β-rays must be attributed to their kinetic energy and ionizing power, not to their own charges, which in comparison with the secondary charges produced are wholly insignificant."

Experiments were also conducted on the rates of heating of water and of colloids under cathode-ray bombardment. One junction of a copper–

constantan thermocouple was kept in ice, and the other was placed in the liquid above the level of the direct cathode ray stream; the heating produced was measured by deflections of a sensitive galvanometer. During the latter part of this work the reaction cell consisted of two circular sheets of mica 5 cm. in diameter and 0.0025 cm. thick cemented to a ring of glass 0.63 cm. thick, and supported by a thin circular brass strip held in a wooden clamp. This apparatus was designed to have as small a water equivalent as possible. The results obtained are shown in table 3.

TABLE 3

Rates of heating of water and of colloids under cathode-ray bombardment

Tube voltage, 155 to 160 kilovolts

COLLOIDAL SOLUTION	TUBE CURRENT	RATE OF HEATING OF SOL RELATIVE TO RATE OF HEATING OF WATER	REMARKS
	milliamperes		
Silver (0.008 g. per 100 cc.)	0.25	1.26	Conditions as nearly uniform as possible
Silver (0.008 g. per 100 cc.)	0.21	1.09	
Gold (0.038 g. per 100 cc.)	0.18	1.32	
Copper (0.009 g. per 100 cc.)	0.18	1.32	
Gold (0.038 g. per 100 cc.)	0.18	1.06	Position of cell changed relative to window
Copper (0.010 g. per 100 cc.)	0.18	1.14	Readings taken on successive days
Copper (0.010 g. per 100 cc.)	0.18	1.12	
Gold (0.0322 g. per 100 cc.)	0.18	1.31	
Gold (0.0322 g. per 100 cc.)	0.15	1.12	Conditions as nearly uniform as possible
Gold (0.0322 g. per 100 cc.)	0.15	1.10	
Gold (0.0256 g. per 100 cc.)	0.15	1.17	Conditions as nearly uniform as possible
Gold (0.0256 g. per 100 cc.)	0.15	1.15	

* Each of the last five results represents the average of two sets of experiments performed consecutively.

In each case investigated the rate of heating of the sol was greater than the rate of heating of the water; the rates of heating were approximately proportional to the tube current; and the rates of heating of sols on different days under similar conditions were in very good agreement.

The results seem quite definite, but the explanation must be a matter for further research. Intensity measurements indicate that both the water and the sol completely absorb the energy of the cathode ray beams bombarding the liquid, and theoretical calculations show that on passing through the cell the intensity of the cathode ray stream is reduced to 10^{-28} of its initial value. The accepted heats of flocculation are 10^3 times too small to account for the observed differences, the energy due to the charge on the surface of the colloid particles is 10^6 times too small, and the energy due to the compression of the water around the colloid particle is about 10^{13} times too small; so that it is not at all clear what additional source of energy in the colloid state could account for this phenomenon.

SUMMARY

1. The stability of both positively and negatively charged sols is decreased by exposure to cathode rays.
2. This result is in agreement with the theoretical considerations outlined.
3. The rate of heating of a sol under cathode ray bombardment is slightly greater than the rate of heating of water under similar conditions. Known sources of energy in the colloid state are found inadequate to account for this phenomenon.

In conclusion, the author wishes to express her sincere appreciation to Professor E. F. Burton and to Professor H. J. C. Ireton, of the Department of Physics at the University of Toronto, for their helpful suggestions and advice throughout the investigation.

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MIGRATION STUDIES WITH COLLOIDS. III

The Behavior of Gelatin-protected Ferric Oxide and Manganese Dioxide Sols

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INTRODUCTION

A characteristic of hydrophilic sols in general, and gelatin in particular, is that they show a diffuse light cone and no "resolvable" particles when viewed under the ultramicroscope. It has been found easier, therefore, to abandon the use of this instrument when making electrophoretic studies with these systems (8, 22, 24, 26, 28). Particles of microscopic size have been suspended in protein sols and their rate of movement in an electric field measured with the aid of a microscope (3, 8, 18a). It has been shown that the particles are coated with an adsorbed film of protein (5, 16; see, however, references 4 and 25), and that their behavior in an electric field is due entirely to the protein covering.

In the present investigation it has been found that the particles in ferric oxide–gelatin sol mixtures and manganese dioxide–gelatin sol mixtures are "visible" in an ultramicroscope, and that their migration velocities under varying conditions can be studied.

EXPERIMENTAL

The ferric oxide sol was made by high temperature hydrolysis of a ferric chloride solution and was dialyzed for a week at 90°C. It was diluted to 0.5 g. of iron per liter for use in preparation of the samples. The manganese dioxide sol was prepared by adding concentrated ammonium hydroxide to boiling potassium permanganate (7) and dialyzing as above.

Stock solutions of gelatin were made from day to day with Eastman de-ashed gelatin. This was dissolved at 50°C. and cooled to room temperature, after which a trace of toluene was added as a preservative.

In the study of the effect of salts on the migration velocity of sol–gelatin mixtures, stock samples were made by adding 0.1 per cent gelatin to the sol in the ratio of 4 cc. to 1 cc. Individual sol–gelatin–electrolyte samples were prepared by adding 50 cc. of electrolyte solution to 50 cc. of the above sol–gel mixture. Before any observations were made the samples were set aside for about half an hour to permit equilibrium to be established.

Migration velocities were determined by a method previously described (11). Measurements of pH were made with the glass electrode at approximately the same time as the migration velocities.

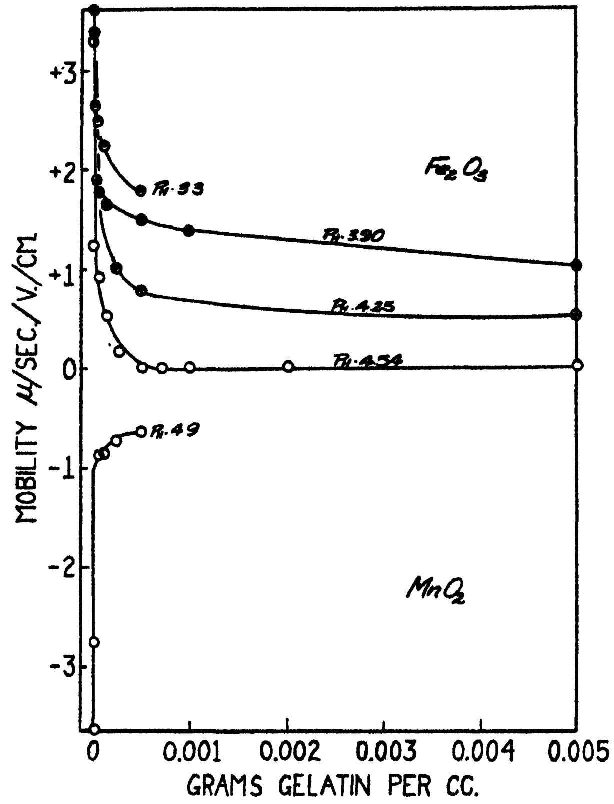

FIG. 1. EFFECT OF GELATIN CONCENTRATION ON FERRIC OXIDE AND MANGANESE DIOXIDE PARTICLES

The effect of gelatin on the migration velocity of ferric oxide and manganese dioxide sols

Some of the results with ferric oxide and gelatin are plotted in figure 1, where it is shown that a limiting value of the electric mobility is approached at about 0.002 g. of gelatin per cm.^{3} Samples were made as follows: 10 cc. of sol of the desired pH was diluted to 50 cc. with water of the same pH, and to this were added varying amounts of a 0.1 per cent gelatin solution made up to 50 cc. with water, all of the same pH. The hydrogen-ion activities were adjusted with hydrochloric acid. Results similar to these have been obtained by Limburg (15), who investigated the relation between the pH value of gelatin and its efficiency as an emulsifier for pure paraffin oil. Limburg made measurements of the cataphoretic velocity of the oil at pH 2.8, 4.7, 5.5 and 9.6, as a function of the concentration of the gelatin. When sufficient gelatin was added, a steady minimum for the migration velocity was reached for any given pH. At pH 4.7 this value was zero.

It has been shown frequently that albumin added in the proper proportions to hydrophobic sols sensitizes and even precipitates the latter (6, 10, 21, 23). Freundlich studied a ferric oxide–crude egg albumin sol and a Carey Lea silver–gelatin sol (9), and observed in both cases that in the presence of small amounts of protein the mobilities of the hydrophobic sols were decreased and the sols coagulated. He further found that increased amounts of gelatin stabilized the silver–gelatin mixture. This author considered that the particles of the hydrophobic sol were enveloped by micells of protein, and that the positive groups of the ampholyte ions were adsorbed by the negative silver particles while the negative groups projected into solution.

Discharge of the system at pH 4.56 led to coagulation at several of the higher concentrations of gelatin. Since at this hydrogen-ion concentration the charge on the gelatin is either neutral or slightly positive, and, in the latter case, of the same sign as the ferric oxide, it would seem that the conditions do not favor an explanation on the basis of mutual coagulation as suggested by Thomas (27). A possible explanation of the precipitation is that owing to the close proximity of the gelatin to its isoelectric point its solubility is near the minimum and when some of the soluble groups are removed from solution by adsorption, the gelatin precipitates with the discharged ferric oxide.

The effect of hydrogen-ion concentration on the mobility of particles in sol–gelatin mixtures

Various minima and maxima properties of gelatin are identified with its isoelectric point. Changes in the magnitude of these properties with pH are associated with its ampholyte behavior, e.g., alteration of the degree of ionization of the acid and basic groups with the acidity of the system. In addition to change of ionization produced by varying the acidity there is evidence (12, 13, 14) that the hydrogen ion also produces changes in the degree of dispersion of the gelatin particles.

Loeb (18) laid great stress on the importance of hydrogen-ion concentration in protein behavior; the correctness of this viewpoint was amply borne out by experiments with gelatin in the present investigation.

The marked influence of hydrogen-ion activity on the mobility of sol–gelatin mixtures is shown in figure 2. The samples were prepared in a uniform manner by mixing 10 cc. of sol with 40 cc. of a 0.1 per cent gelatin solution and diluting with 50 cc. of water, all of the same pH. The fact that in the presence of gelatin the two oppositely charged hydrophobic sols give a single curve strongly indicates that the systems consist of gelatin-coated particles and that their behavior is that of the protein. The concentration of gelatin in these experiments was 0.0004 g. per cubic centimeter, and is sufficient to cover the particles of the metallic oxide hydrosols with a film of protein. These results may be compared with those of Abramson (1), who also found that concentrations of the order of 10^{-4} g. of gelatin per cubic centimeter were able to convey to quartz particles the properties of the protein.

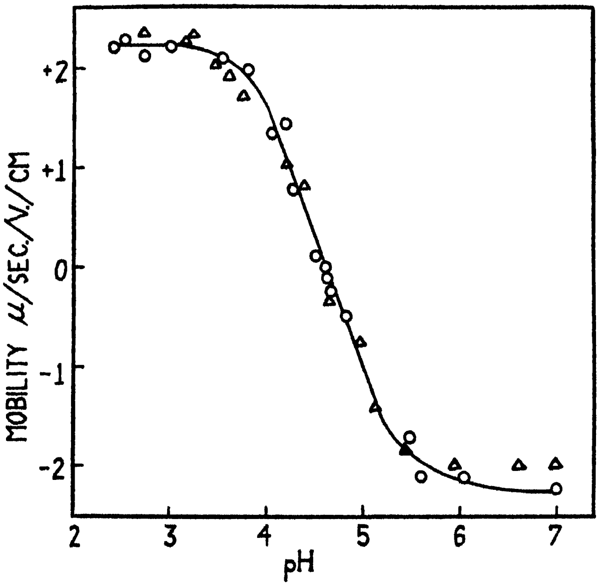

FIG. 2. EFFECT OF HYDROGEN-ION ACTIVITY ON GELATIN-COATED FERRIC OXIDE AND MANGANESE DIOXIDE PARTICLES

○ Fe_2O_3 sol; △ MnO_2 sol

The effect of salts on the migration velocity of sol–gelatin mixtures

When salts of the type KCl, K_2SO_4, KH_2PO_4, and $K_3Fe(CN)_6$, are added to a ferric oxide sol, pH 3.9, it is found that there are marked differences in the ability of the salts to decrease the migration velocity of the particles. Potassium chloride, which furnishes the weakly adsorbed chloride ion, decreases the mobility of ferric oxide particles very slightly. With potassium sulfate the discharging by the bivalent sulfate ion is much more pronounced. Monopotassium phosphate and potassium ferricyanide produce a still greater lowering of the mobility and recharge the ferric oxide to the negative form at low concentrations of the electrolyte.

On the other hand, when these same salts are added to a sol–gelatin mixture pH 3.9, it is found (figure 3) that the mobility curves lie close together and that the marked differences in discharging power associated with mono-, di- and tri-valent ions are absent. It is apparent, however, that there exists a slight increase in the ability of the ions to lower the mobility of the particles as the valence of the negative ion increases. The discharge curves for potassium chloride and monopotassium phosphate are practically identical, indicating that the phosphate ionizes as a monovalent ion. This is in contrast to the behavior of the salt with unprotected ferric oxide, where it acts as though ionized into trivalent phosphate ions, but is in accord with the experiments of Loeb who found that this salt acted as a monovalent ion with the proteins.

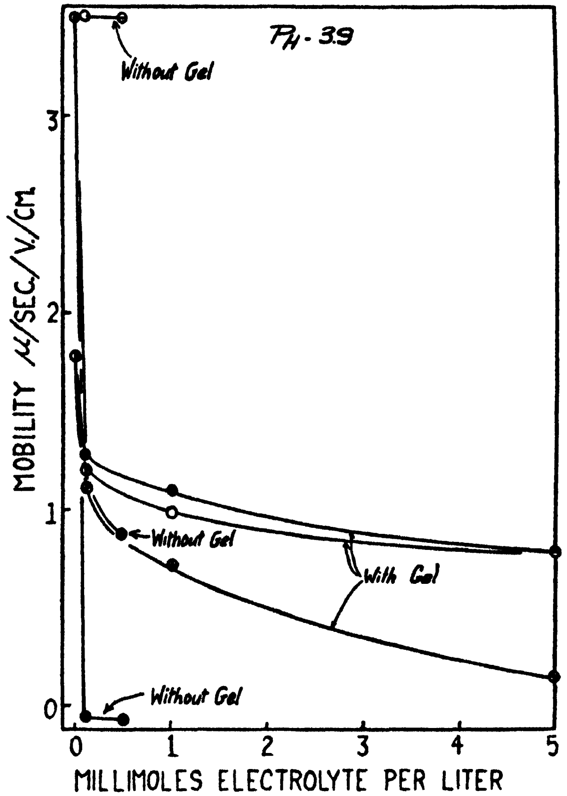

FIG. 3. COMPARISON OF THE EFFECT OF ELECTROLYTES ON UNPROTECTED FERRIC OXIDE AND ON GELATIN-PROTECTED FERRIC OXIDE

○ KCl ● KH_2PO_4 ⊕ K_2SO_4

Addition of the electrolytes to a sol–gelatin system of pH 3.9 produced a decrease in acidity of the system. It was found, subsequently, that the major part of the effect of these salts in lowering the mobility of the particles was due to the pH change. However, the latter is corrected for in figures 4 to 11, and it is evident that there remains a real discharging action by the ions of the electrolytes themselves. The migration data in each figure are for a single electrolyte. Three different concentrations of the salt are plotted at several different pH values. The dotted curve represents the migration velocity in the absence of electrolyte, i.e., the effect of hydrogen-ion activity on the mobility. The divergence of the curves from the dotted line represents the discharging effects of the electrolytes, the order being, for ferric oxide–gelatin, $K_3Fe(CN)_6 > K_2SO_4 >$ KCl, KSCN, KH_2PO_4. With the possible exception of monopotassium phosphate the order is the same expected with any positive sol.

In this connection the thing that distinguishes a positive ferric oxide–gelatin system from colloidal systems without gelatin is that the chloride ion produces a lowering of mobility much greater than is to be expected from the well-known low adsorbability of monovalent ions, and also that the sulfate and ferricyanide ions produce a smaller decrease in velocity than is associated with their high adsorbabilities.[1]

DISCUSSION

It is usually adduced from acid and base titration data with the proteins and from the close agreement between the mobilities of freely dispersed proteins as compared with the mobilities of protein-coated surfaces that all of the polar groups are free after adsorption has occurred (2). Thus the fact that the mobility curves of gelatin-coated ferric oxide particles (initially positive) and manganese dioxide particles (initially negative) are the same (figure 2) indicates not only that the mobilities are a function of the protein surface but also suggests, since the isoelectric point (pH about 4.6) under these conditions is in fair agreement with values frequently observed with freely dispersed gelatin, that adsorbed gelatin has ionizing properties similar to dissolved gelatin. However, if gelatin is to be regarded as a polyvalent electrolyte of high molecular weight (which properties together with its degree of ionization are related to the hydrogen-ion activity of the system), one would expect it to be highly adsorbable. The course of the curve in figure 2 might then be interpreted on the premise that gelatin is so strongly adsorbed through its polar groups by hydrophobic particles that the latter acquire a mobility close to the ionic mobility of the dissolved protein. The results in figure 1 are not entirely consistent with a mechanism of adsorption in which polar groups do not take part. The data in this figure show the decrease in mobility of iron oxide with increasing amounts of gelatin. The curves are typical in form to those

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[1] There is no reason to question that gelatin adsorbs ions, but from the present data the mechanism of this adsorption does not appear to be one in which the ions enter directly into the double layer, i.e., to decrease its thickness.

Fig. 4

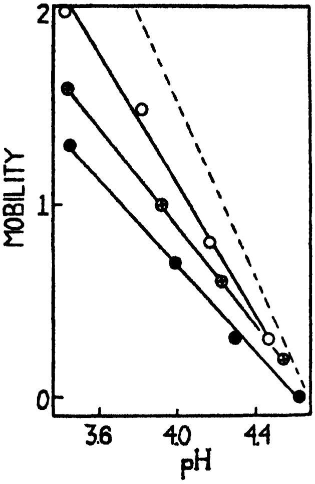


Fig. 5

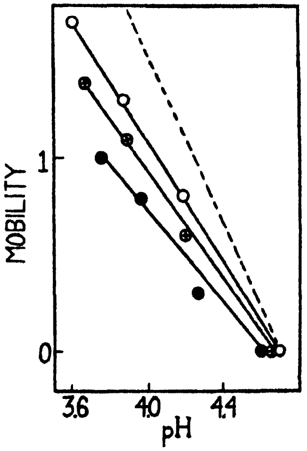


Fig. 6

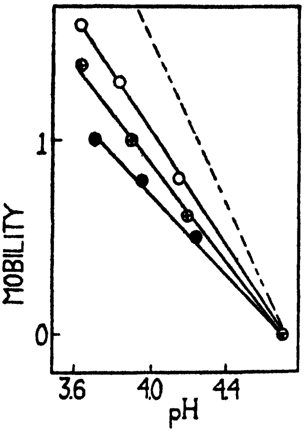


Fig. 7

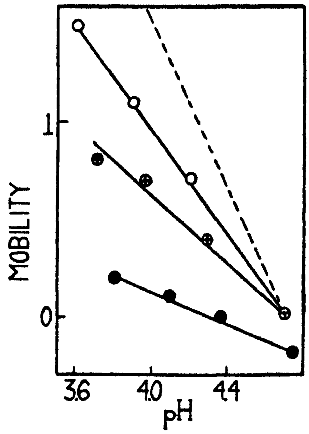


Fig. 4. Ferric Oxide–Gelatin

○ KCNS, 0.1 millimole per liter
⊕ KCNS, 1.0 millimole per liter
● KCNS, 5.0 millimoles per liter

Fig. 5. Ferric Oxide–Gelatin

○ KH_2PO_4, 0.1 millimole per liter
⊕ KH_2PO_4, 1.0 millimole per liter
● KH_2PO_4, 5.0 millimoles per liter

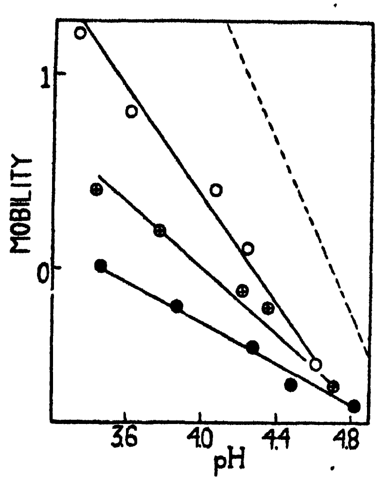
Fig. 6. Ferric Oxide–Gelatin

○ KCl, 0.1 millimole per liter
⊕ KCl, 1.0 millimole per liter
● KCl, 5.0 millimoles per liter

Fig. 7. Ferric Oxide–Gelatin

○ K_2SO_4, 0.1 millimole per liter
⊕ K_2SO_4, 1.0 millimole per liter
● K_2SO_4, 5.0 millimoles per liter

Fig. 8



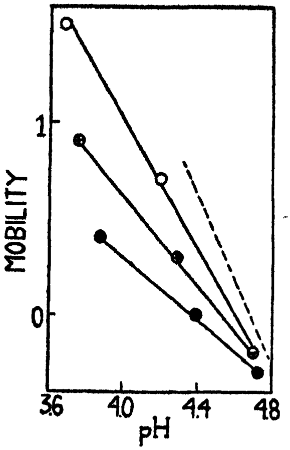
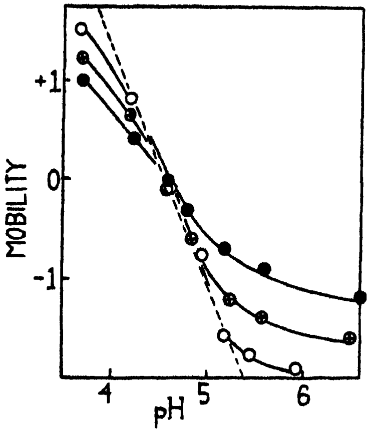


Fig. 9

Fig. 10



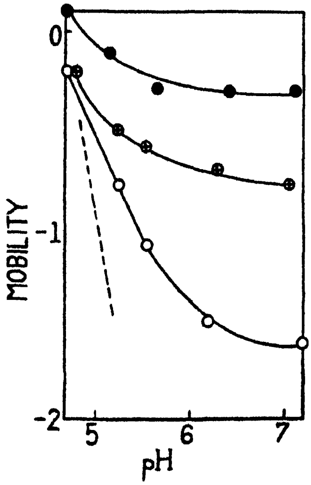


Fig. 11

Fig. 8. Ferric Oxide-Gelatin

○ $K_3Fe(CN)_6$, 0.1 millimole per liter
⊕ $K_3Fe(CN)_6$, 1.0 millimole per liter
● $K_3Fe(CN)_6$, 5.0 millimoles per liter

Fig. 9. Manganese Dioxide-Gelatin

○ K_2SO_4, 0.1 millimole per liter
⊕ K_2SO_4, 1.0 millimole per liter
● K_2SO_4, 5.0 millimoles per liter

Fig. 10. Manganese Dioxide-Gelatin

○ KCl, 0.1 millimole per liter
⊕ KCl, 1.0 millimole per liter
● KCl, 5.0 millimoles per liter

Fig. 11. Manganese Dioxide-Gelatin

○ $BaCl_2$, 0.1 millimole per liter
⊕ $BaCl_2$, 1.0 millimole per liter
● $BaCl_2$, 5.0 millimoles per liter

obtained when electrolytes are added to colloidal ferric oxide and where it is assumed from classical theory that the ions of the electrolyte are adsorbed, i.e., enter into and decrease the thickness of the double layer.

Loeb (19) has shown that the solubility of gelatin is increased by the addition of salts. He has also shown (17) that collodion particles coated with isoelectric gelatin are unstable, but that they are stabilized by small amounts of salts without altering their cataphoretic velocity from zero. Results comparable to these were obtained with iron oxide and gelatin, where it was found that isoelectric mixtures are unstable but that low concentrations of salts produce stability. A possible explanation for the effect of small amounts of electrolytes is that they disperse the gelatin into smaller particles, rendering possible the formation of more soluble groups per unit weight of protein.

The stock solutions of electrolytes used in this study were all of a concentration of $M/100$. It was found that when the acidity of an electrolyte was adjusted to pH of about 4 and then added to an equal volume of a 0.1 per cent gelatin solution of the same pH, the mixed system became more alkaline. The pH change occurred rapidly and without hysteresis. Similar results were obtained with other electrolytes, although the increase was not always the same for different electrolytes. When the hydrogen-ion activities were on the alkaline side of the isoelectric point, the mixed systems were more acid than either of the constituents. Thus it would seem that the changes in hydrogen-ion activity are not due solely to alteration in ionic strength of the solution (since the pH is shifted in opposite directions when the system is on the acid side of the neutral point, pH 7.0). The data are shown in table 1.

Loeb (20) did not give much emphasis to the effect of electrolytes just described, and this fact tends to lend confusion to some of his findings. For example, his results on the mobility of proteins with potassium ferrocyanide are of doubtful significance. It is difficult to hold this salt at a constant pH for any considerable length of time, and, further, when a potassium ferrocyanide solution of a pH such as Loeb used is mixed with gelatin of the same pH there occurs a marked change in acidity with a slow attainment,[2] if any, of equilibrium.[3] In the present work the use of this salt had to be abandoned, although it gave mobility curves similar to Loeb's when only the pH of the original solutions (before mixing) was considered. It should be noted that it does not seem possible to make dilutions with gelatin solutions, electrolyte solutions, and water all of the same pH and obtain a series of samples of the same acidities (unless, possibly, this was done at the isoelectric point).

The order of electrolytes in decreasing the mobility of positive gelatin-coated particles (at a constant hydrogen activity, see figures 4 to 8) is $K_3Fe(CN)_6 > K_2SO_4 > KCl$, $KSCN$, KH_2PO_4. From table 1 it may be observed that this order is identical with the effectiveness of the salts in decreasing the acidity of gelatin when it is on the acid side of the isoelectric point. In neither instance was there any evidence of lyotropy with the monovalent ions.

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[2] With other salts of this study equilibrium was rapidly established.

[3] In this case Loeb noticed a change in pH after eighteen hours.

The change in acidity produced by salts is consistent with the assumption that salts disperse the protein into smaller particles with the resultant increase in total number of active groups. The groups which are released by dispersion are probably in the isoelectric condition when first formed, but quickly adjust themselves to the acidity of the medium. This readjustment uses up acid or base depending upon the original pH of the system. Thus the shift in pH is toward the isoelectric point.

TABLE 1

Changes in pH values when solutions of electrolytes and of gelatin are mixed

ELECTROLYTE	pH BEFORE MIXING	pH AFTER MIXING
Gel	3.91	
KCl	3.83	3.97
K_2SO_4	3.86	4.05
KH_2PO_4	3.86	3.97
$K_3Fe(CN)_6$	3.85	4.17
$BaCl_2$	3.85	3.99
Gel	3.87	
KSCN	3.88	3.98
Gel	4.95	
KCl	4.98	4.88
$BaCl_2$	4.95	4.72

It has been mentioned that gelatin-coated particles of ferric oxide and manganese dioxide have the properties of the protein itself. It is none the less true that addition of an excess of gelatin (figure 1) over the minimum required to give protein properties to a protected particle results in a still further decrease in velocity of the particle. The decrease in mobility is the result of a decrease in the electrokinetic potential. If the addition of neutral salts to gelatin leads to dispersion and an increase in the concentration of ampholyte groups, the salt which produces this change to the greatest degree should be the most effective in lowering the cataphoretic velocity at a given hydrogen-ion concentration. Thus the reason why electrolytes of different valence do not lower the mobility in proportion to their adsorption isotherms may be explained. The addition of ions of different valence does not lead to an entrance of these ions into the double layer but instead results in an increase in the concentration of an ion (gelatin) already present.

In conclusion it may be stated that since molecular weight determinations on gelatin (13) have been made with buffer systems and therefore in the presence of salts, any effects of the latter in producing dispersion would be included with those of the hydrogen ion.

SUMMARY

1. An ultramicroscopic method has been used to study the migration velocity of gelatin-coated ferric oxide and manganese dioxide particles.

2. The effects of concentration of gelatin and of the hydrogen-ion concentration of the system are shown in relation to the mobility of the protected particles.

3. The effects of salts of different valence on the mobility of hydrophobic particles covered with a protein film have been found to be more in direct proportion to their valence than with their adsorption isotherms.

4. When the electrolyte solutions and gelatin were adjusted to the same pH and mixed, the hydrogen-ion concentration was altered. The mixed systems became more alkaline when the original acidity was on the acid side of the isoelectric point and more acid when on the alkaline side of the isoelectric point. The order of electrolytes in altering the hydrogen-ion concentration was identical with their effectiveness in decreasing the mobility of gelatin-protected particles.

5. It has been suggested that small amounts of salts disperse gelatin into smaller particles, liberating more active groups.

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THE STABILITY OF EMULSIONS AS DETERMINED BY THE DISTRIBUTION OF SIZES

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INTRODUCTION

One of the most important characteristics of an emulsion is its stability. This stability has generally been determined by allowing the emulsion to stand until the dispersed phase collects in bulk to an extent decided upon by the individual observer. This method is not only uncertain, but also extremely slow since, for example, emulsions of oil in water prepared in this laboratory have exhibited no separation of oil during a period of five years after their initial preparation. It was suggested by Harkins and Beeman (4) that a determination of the variation of the distribution of sizes of the dispersed droplets of the emulsion with time gives a measure of its stability. Of course, the stability of emulsion systems, like the stability of true colloidal systems, depends not only on the degree of dispersion of the dispersed phase, but also upon certain other factors, such as (1) interfacial tension, which induces the coalescence of globules of the dispersed phase, reducing thereby the total surface, and (2) the electric charge of the globules, tending to repel globules on near approach. As in other colloidal systems, the presence of a large number of small-sized particles characteristic for the permanent state appears to be general. The distribution of sizes for two types of emulsions, octane and heavy paraffin oil (stanolax) in aqueous solutions of sodium oleate, was determined in order to obtain information concerning their stability under various conditions.

APPARATUS AND PROCEDURE FOR OBTAINING NUMBER DISTRIBUTION CURVES

Purification of substances

The accuracy of the determination of the distribution of sizes of the droplets in an emulsion depends not only upon the method used, but also upon the purity of the participating components of the respective system. The purification of the substances used in this investigation and the preparation of the emulsions studied are presented herein in detail.

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It is known that oleic acid, from which oleates used as emulsifiers are prepared, always contains by-products in the form of other fatty acids, and when exposed to air oxidizes readily. Oleates also oxidize readily, but since sodium oleate is oxidized less readily than potassium oleate it was used in the investigation. The method employed for the purification of oleic acid was a modification of one generally recommended: The commercial U.S.P. oleic acid was first shaken with pure granular rice carbon (Kahlbaum). After twenty-four hours standing the oleic acid was filtered from the carbon, water added to form an emulsion, and 0.1 *N* potassium hydroxide solution stirred into this mass until the saponified emulsion dissolved, when a saturated solution of lead chloride was poured in until a white, flocculent precipitate of the lead salts of the fatty acids separated out. The precipitate was filtered, the solution tested for complete precipitation, and the lead salts washed many times by decantation, the water being drawn off by suction on the funnel in the absence of air. These salts were then dissolved in ether by shaking and left standing in ether for four to five days for the complete removal of lead oleate. Other fatty acid salts, such as those of stearic acid, remaining as precipitates in the ether solution were separated by filtration. The lead oleate dissolved in ether was poured into a separatory funnel and repeatedly shaken with fresh portions of 0.1 *N* hydrochloric acid until complete separation was effected. The ether layer was evaporated on a water bath; water was then added to the remaining oleic acid, which was resaponified with 25 per cent ammonia solution, and then diluted with water until all the soap dissolved. Treating with lead chloride does not render the oleic acid completely free from other admixed fatty acids, a small amount always remaining in the ether after the extraction. Therefore the soap solution was treated with barium chloride; a white, flocculent precipitate of barium oleate was obtained, which was allowed to settle for several hours. The precipitate was sucked from the cold solution in the absence of air, the barium oleate decomposed with tartaric acid or hydrochloric acid, and washed to separate the excess of acid. Even after this treatment the purified oleic acid still contained some palmitic and stearic acids, for the complete removal of which the oleic acid was subjected to a fractional distillation.

Oleic acid decomposes, upon distillation under ordinary pressure, into water, carbon dioxide, acetic acid, caprylic acid, capric acid, and elaidic acid; therefore it was distilled under a pressure of 10 to 15 mm. to prevent decomposition (under this pressure oleic acid boils at about 223°C.). The pure oleic acid obtained after final purification was a colorless, odorless liquid, solidifying at a low temperature and in the solid state melting at 14°C. Sodium oleate was then prepared from the purified oleic acid.

Pure metallic sodium was dissolved in pure ethyl alcohol and a calculated amount of oleic acid previously dissolved in ethyl alcohol added to the sodium ethylate until repeated tests of the alcoholic solution indicated a neutral reaction with a boiling mixture of three parts of alcohol and one part of water containing a few drops of phenolphthalein. The neutral alcoholic solution was evaporated on a water bath to dryness, the residue dissolved in absolute alcohol and refluxed for one hour. The hot solution was filtered through a hot air funnel. The soap obtained was crystallized, the crystals washed well with alcohol and dried in air. The dry powder was rubbed in a mortar with pure absolute ether until the fine soap powder was free from impurities; the ether was then removed by suction. The sodium oleate, obtained in the form of a white powder, was dried over phosphorus pentoxide in a vacuum desiccator for the elimination of water and ether, and ground to extreme fineness; its melting point was found to be 230–232°C., corresponding to that of pure sodium oleate.

Preparation of emulsions

At a definite temperature, an equal volume of the corresponding oil flowing in a thin stream from a pipet was added to an aqueous soap solution stirred by an Arnold drink mixer in a tube with a flat bottom at a constant speed of 3500 revolutions per minute. The emulsion obtained was homogenized by drawing it up into a large 100-cc. pipet by means of a suction pump and rapidly expelling it by compressed air. This operation was repeated five times. Foaming did not occur when the homogenization proceeded comparatively slowly. The emulsion was poured into 10-cc. measuring cylinders having flat bottoms and provided with glass stoppers to prevent evaporation.

Apparatus

The apparatus used for the determination of the distribution of sizes of globules in emulsions was a new type Leitz microprojection equipment with a special collimator of great light-transmitting power. The emulsion was protected from the heat of the arc lamp by the use of a cell containing a solution of ferrous ammonium sulfate to which had been added a few drops of sulfuric acid to prevent its oxidation on exposure to air, also by a green-gold glass (patented) fixed on the wall of the heat-adsorbing cell. In addition, the microscope stand was surrounded by a series of lead tubes of small diameter in which cold water circulated. In this way, drying of the emulsions used in protracted experiments was prevented.

EXPERIMENTAL PART

All emulsions prepared as previously mentioned and before observation under the microscope were diluted three hundred times with distilled water. By means of a projection prism above the ocular, the image obtained in the microscope was projected on a screen made up of a large sheet of millimeter graph paper attached to a wall opposite the projection prism. The distance of the microscope from the screen was such that each millimeter of the graph paper corresponded to one micron (micrometer calibration). The cell containing the emulsion was identical with that used by Harkins and Beeman (4). Special attention was given to the cleaning of the slide with the cell (similar in construction to a hanging drop slide) which served as the container of the emulsion, as well as the cover glasses. The slide and cover glasses were placed in a cleaning solution for several hours, washed many times with distilled water, and then placed in the funnel of an Ostwald boiler containing distilled water and a solution of potassium permanganate, where they were left for an hour under steam. The fact that the slide and cover glasses when taken from the funnel were not wetted by water and dried quickly was evidence that their surfaces were clean.

The distribution of sizes of globules in emulsions was obtained by calculating the number of droplets of various sizes. The method of obtaining the distribution curves of sizes was a statistical method, using the law of great numbers to increase the probability. Each distribution curve was obtained by calculating and measuring an average of fifteen hundred to two thousand droplets. From the calculated number of droplets of each size and the total number of droplets calculated, the percentage of droplets of each size was determined.

The observation procedure was as follows: Immediately after diluting the emulsion, a sample was pipetted from it, placed upon a slide and covered with a cover glass. Oil contacts between the condenser and the slide and between the cover glass and the objective were made with stanolax, since it is more readily cleaned off than cedar oil and does not harden after exposure to air as does cedar oil, which is usually used. Because of the dilution of the emulsion, only a few droplets were present in the microscopic field. The slide containing the emulsion was moved from one side to the other by means of a modified movable stage operated at a distance, and observations were made, after which the slide was cleaned and refilled with a fresh portion of the diluted emulsion. This procedure was repeated for every curve plotted, fifteen hundred to two thousand globules being measured for every curve.

DISCUSSION

Number distribution curves were obtained for octane–water and stanolax–water emulsions with sodium oleate as the emulsifier. The effects produced by varying the concentration of the emulsifier, and particularly those changes in the distribution with time, were studied in order to draw a relationship between the distribution of sizes of the dispersed phase and the stability of the emulsion system. The figure with curves obtained for the distribution of sizes of oil droplets in octane–water and stanolax–water emulsions showed clearly: (1) that the maximum number of droplets corresponding in size from 1 to 1.5 microns in diameter is independent of the concentration, high or low, of the emulsifier used to produce a relatively permanent emulsion, and of the age of the emulsion, whether it is a day, a month, or even years since its initial preparation; (2) that the distribution of intermediate size droplets is rather gradual; (3) that deviations in both directions from the maximum size droplets correspond to the peak in the number distribution curve prior to the establishment of a stable static equilibrium of the emulsion, e.g., the course of changes in the distribution of sizes being comparable to the swing of a pendulum at both its extremities; (4) that this method of attaining a state of equilibrium indicates changes occurring in the distribution of sizes with time by the ageing of the emulsion systems and varies with various concentrations of the emulsifier; (5) the percentage of large size droplets, such as those from 10 to 30 microns in size, was extremely small, very few being present in stable emulsion systems, and their appearance indicates a transition to an unstable form (the unstable state was verified by the distortion of the perfectly round shape of the droplets); (6) that the maximum peak in the distribution curve appeared not to be displaced by using a viscous oil instead of a fluid oil in an emulsion.

These are the general results derived from a casual perusal of the data obtained and tabulated with respect to the distribution of sizes of droplets in different emulsion systems in the investigation of which factors influencing their state of permanency were varied.

To study more thoroughly the kinetics of changes as reflected in the distribution of sizes, it was necessary to pursue small rates of changes of the physical quantity; therefore a mathematical analysis of the results obtained was necessitated. The distribution of sizes and the corresponding percentage of droplets obtained experimentally were plotted for each emulsion directly in a coördinate system as integral curves, and from these integral curves derivative curves were constructed. For the evaluation of the derivative $y' - \frac{dy}{dx}$ when the function is known analytically, a differential calculus or a graphical method must be used. Geometrically, the procedure consists in using the principle that the ordinate of the derivative curve at any point $P'(x, y)'$ is equal to the slope of the integral curve at any point, that is, of the tangent at the corresponding point of the integral curve.

The practical construction of the derivative curve is as follows (figure 1): A point S $(-2, 0)$ is chosen at a convenient distance to the left of the axis y and a line parallel to the tangent drawn for each point of the integral curve. This parallel cuts the ordinate axis at the point U. Since SU forms with the axis $+x$ the same angle α as the tangent t, then $OU = \text{tg}\alpha = y'$ and the point *U* projected horizontally on the ordinate from the point *P* cuts it at *P'*, which is the point of the derivative curve corresponding to the point *P* of the integral curve. Since $Y' = 1/a\int y.\mathrm{d}x$, then $\mathrm{d}y/\mathrm{d}x = 1/aY$. The slope of the integral curve at any point is proportional to the ordinate of the derivative curve at the corresponding point. Derivative curves for all integral curves were constructed in this manner.

In comparing derivative curves (figure 2, 0.10 *M* sodium oleate–octane–water emulsions) corresponding to integral curves expressing a change in the distribution of sizes with time as the emulsion grows older, it is seen that derivative curves *A'* and *C'* of aged emulsions have a large number of small size droplets, the maximum not even being indicated. Emulsions one day old and seven days old, respectively, differ from aged emulsions in the shape of the distribution curve in that their maximum is extended, *D'* indicating that there are several sizes of droplets in the maximum region, while *B'* limits the maximum to globules of certain definite size. The percentage of maximum (number) of globules of large sizes is more pronounced in aged emulsions.

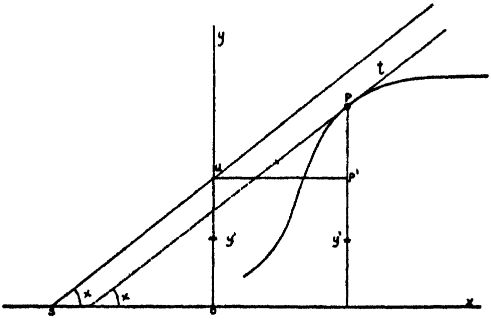

FIG. 1. GRAPHICAL METHOD FOR DERIVING DIFFERENTIAL CURVES

Figure 3 presents the same kind of derivative curves for the corresponding integral curves as figure 2, 0.10 *M* sodium oleate–octane–water emulsions, except that 0.01 *M* sodium hydroxide was added for the prevention of hydrolysis usually occurring in these emulsions (1). It was interesting to note the effect of an alkali, added to counteract hydrolysis, on the character of the distribution of sizes in these emulsions, it being found that the dispersion into finer droplets was favored by the addition of alkali and that the distribution curves for emulsions in which hydrolysis was compensated reshaped the derivative curve, that is, a curve with an unexpressed maximum lying in an unmeasurable region (ultramicrons). Depending on the amount of alkali added, hydrolysis is retarded for varying periods of time, and the stability of emulsions containing an excess of alkali is not essentially improved in comparison with emulsions to which no alkali has been added for, after two months, the maximum level of small size droplets decreases markedly and is almost equal to that of emulsions without alkali (compare figure 3 with figure 2).

A comparison of figure 3 with figure 2 makes evident also that the effect

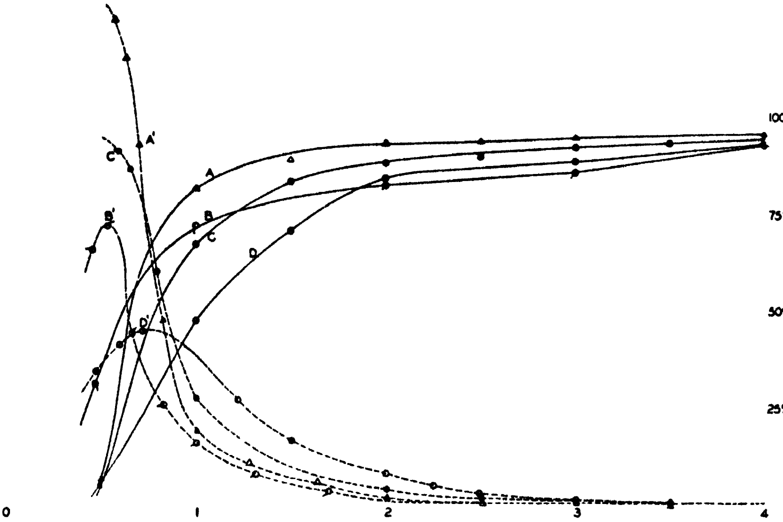

FIG. 2. 0.10 *M* SODIUM OLEATE–OCTANE–WATER EMULSIONS
△, AA′, 12 days old; ρ, BB′, 7 days old; ●, CC′, 2 months old; ○, DD′, 1 day old

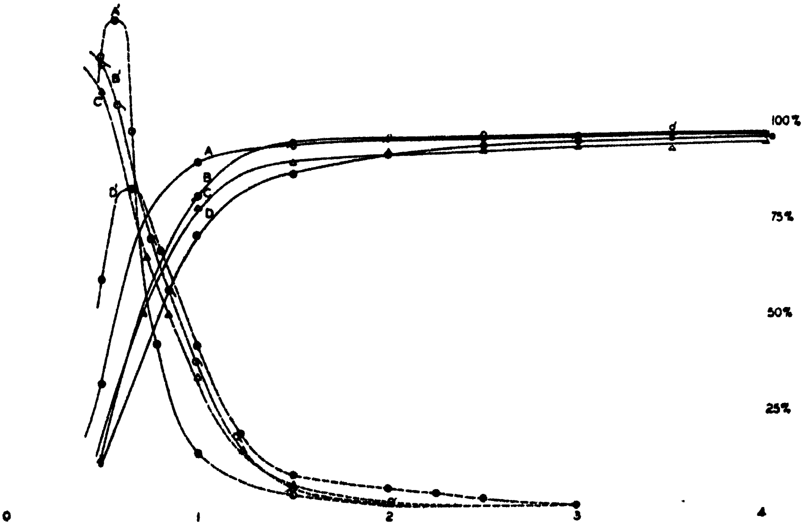

FIG. 3. 0.10 *M* SODIUM OLEATE–OCTANE–WATER EMULSIONS (+ 0.01 *M* SODIUM HYDROXIDE)
○, AA′, 2 days old; ρ, BB′, 9 days old; △, CC′, 13 days old; ●, DD′, 2 months old

of hydrolysis at this concentration (0.10 *M*) of the emulsifier is sharply pronounced immediately after preparing the emulsion, for it interferes with the dispersing factor. However, as time passes, hydrolysis neither affects nor depresses the state of stability.

Figure 4 presents the rate of changes in the integral curves of size distribution when a smaller amount (0.05 *M* sodium oleate) of the emulsifier is used to produce an emulsion system. The percentage of maximum small size droplets continues in the same direction, and as time goes on an equilibrium is established and stability becomes more pronounced. After a period of two months hydrolysis interferes greatly with the stability, the level of the maximum of small size droplets is displaced, and the emulsion exhibits a smaller percentage of small droplets and greater instability.

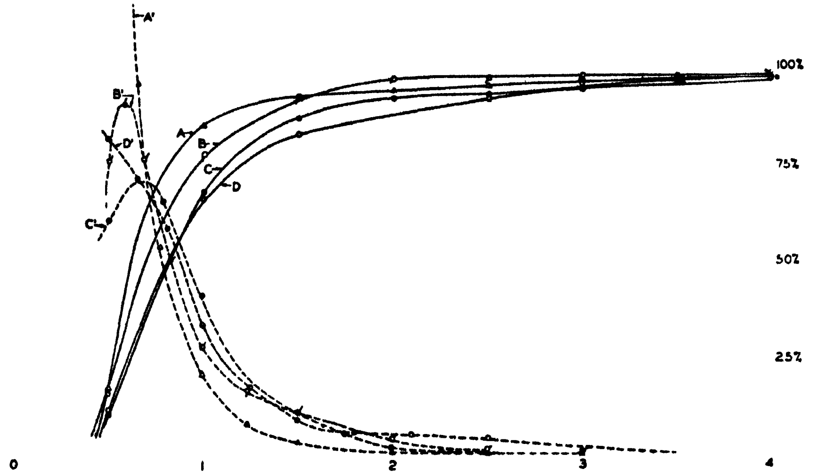

FIG. 4. 0.05 *M* SODIUM OLEATE–OCTANE–WATER EMULSIONS
△, AA′, 12 days old; ρ, BB′, 7 days old; ●, CC′, 2 months old; ○, DD′, 4 days old

A comparison of figure 2 with figure 4 (emulsions of the same age but having different amounts of the emulsifier) shows that curves A′ (twelve days old) have identical shapes indicating stability and the absence of hydrolysis. Curves B′ (seven days old) have an expressed maximum effect of hydrolysis, and the percentage of small size droplets is slightly higher in the case of the lower concentration of the emulsifier. In figure 2, curve C′ (two months old) has a shape suggesting the absence of hydrolysis, while in figure 4, curve C′ (two months old) suggests the presence of hydrolysis; the maximum of small size droplets is displaced to a lower level in the case of the lower concentration of the emulsifier.

With a concentration 0.05 *M* of the emulsifier, no marked hydrolysis is apparent after four days, while with a concentration 0.10 *M* the level of the maximum of small size droplets is the lowest, that is, hydrolysis is present and the emulsion is practically instable. Figure 5 illustrates the ageing process of octane–water emulsions with a still smaller amount of the emulsifier, 0.01 *M* sodium oleate. Curves A′, C′, and D′ exhibit a flat maximum, indicating the least stability of these emulsions. The percentage of the small size droplets increases with time and hydrolysis ceases its interference with the presentation of the actual distribution of sizes, an equilibrium apparently being established between dispersion; later, the action of hydrolysis is reëstablished. The curve obtained for a three-months old emulsion is typical of a stable emulsion in which no hydrolysis has occurred.

In the consideration of a still lower concentration of the emulsifier, the reverse with regard to stability is seen. The amount of the emulsifier seems to be insufficient in maintaining the stability of an emulsion, although readily attained in the beginning; after three days the emulsion has a high per cent of small droplets.

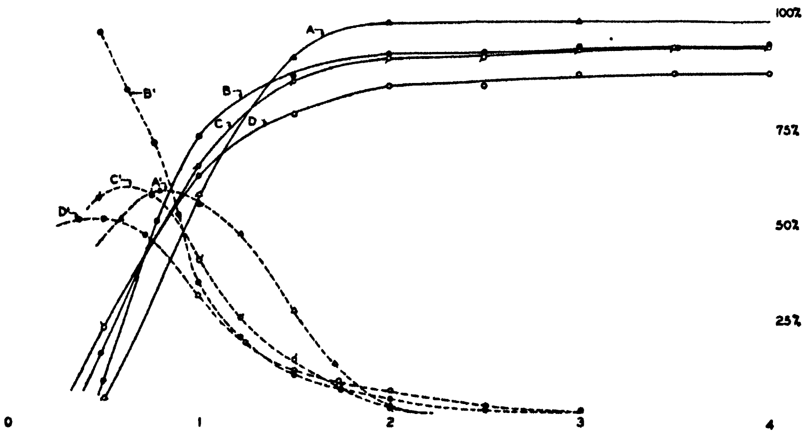

FIG. 5. 0.01 *M* SODIUM OLEATE–OCTANE–WATER EMULSIONS
△, AA′, 2 months old; ●, BB′, 3 months old; ρ, CC′, 15 days old; ○, DD′, 2 days old

Figure 6 presents curves for 0.005 *M* sodium oleate–octane–water emulsions. The shape of the derivative curves changes greatly. In a comparatively short time, after fifteen days, curve C′ has a very extended maximum peak and the percentage decreases rapidly. With an emulsion one month old, curve B′ is obtained, the shape of which is similar to that of a fifteen-day old emulsion, but the decrease in per cent is more gradual and to a lesser extent. It must also be emphasized that emulsions containing a very small amount of the emulsifier are short-lived, lasting only about one month. There is a great resemblance between the shape of curves

A′, C′ of figure 5 and B′, C′ of figure 6, but a striking difference between D′ of figure 5 and A′ of figure 6. That is where the amount of the emulsifier, and correspondingly the weakening in the stabilization action, becomes sharply pronounced.

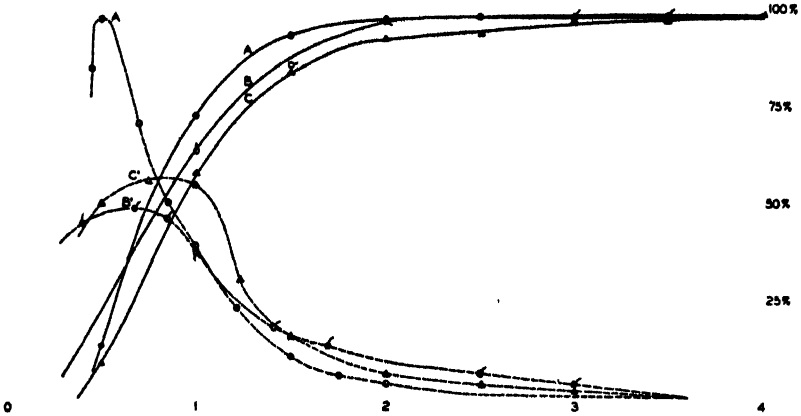

FIG. 6. 0.005 M SODIUM OLEATE–OCTANE–WATER EMULSIONS
○, AA′, 3 days old; ρ, BB′, 1 month old; △, CC′, 15 days old

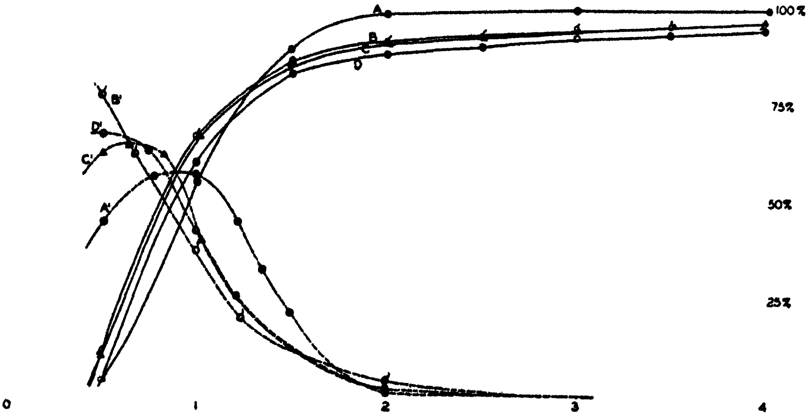

FIG. 7. OCTANE–WATER EMULSIONS (TWO MONTHS OLD)
●, AA′, 0.01 M sodium oleate; ρ, BB′, 0.10 M sodium oleate + 0.01 M sodium hydroxide; △, CC′, 0.05 M sodium oleate; ○, DD′, 0.10 M sodium oleate.

Figure 7 shows the influence of the amount of the emulsifier as compared for emulsions of the same age and when the state of equilibrium has been definitely established, namely, two months after the initial preparation. It is obvious that with an increase in the concentration of the emulsifier a higher maximum level for the per cent of small size droplets is obtained.

D′ > C′ > A′ for 0.005 *M* (measured only for a one-month old emulsion). In addition, the most stable emulsion in this series of increasing stability with the concentration of the emulsifier is the emulsion corresponding to 0.10 *M* sodium oleate plus 0.01 *M* sodium hydroxide; in other words, an emulsion in which hydrolysis has been retarded.

STANOLAX–WATER EMULSION

For the first time in the history of emulsion investigation, emulsions four and five years old have been investigated with regard to their stability, using the method of following the changes in the distribution of sizes in emulsion systems as a means for detecting small rates of changes in their permanency. The emulsions investigated were prepared by Harkins and Beeman four and five years prior to undertaking the present investigation.

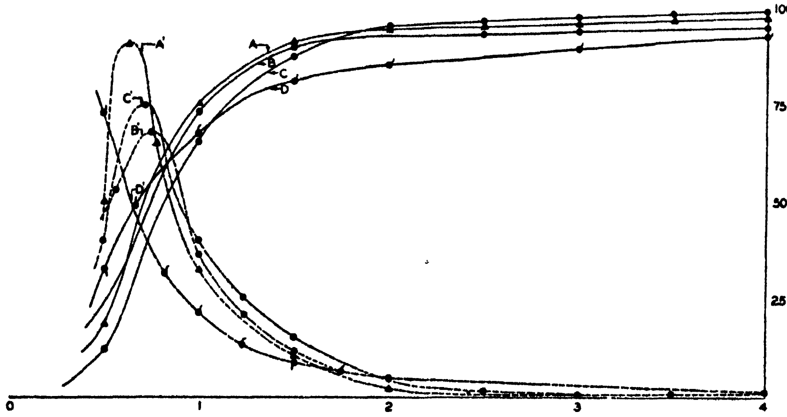

FIG. 8. STANOLAX-WATER EMULSIONS

△, AA′, 0.10 *M* sodium oleate, seven days old; ○, BB′, 0.10 *M* sodium oleate + 0.05 *M* oleic acid, five years old; ●, CC′, 0.10 *M* sodium oleate, forty-one days old; ρ, DD′, 0.10 *M* sodium oleate, four years old.

As may be seen from figure 8, curves B′ and D′ still retain the same shape as those for freshly prepared emulsions under the same conditions. But in comparing them with A′ and C′, the level of maximum size globules is displaced towards the lower one for old age emulsions. The emulsion for curve B′, containing oleic acid to prove the influence of electrolytes, showed a hydrolysis similar to that of a freshly prepared emulsion, while the emulsion (four years old) for curve D′, without the addition of an acid, had a shape typical of permanent emulsions without hydrolysis.

Figure 9 summarizes the results of the investigation on stanolax–water emulsions by varying the concentration of the emulsifier. The influence of the amount of the emulsifier used is pronounced in this case also, that is, in the same direction as was the case with the fluid octane oil which is less viscous than the heavy paraffin oil stanolax. The stability, as well as the larger per cent of small droplets in the dispersed phase of the emulsion, increases with an increase in the amount of the emulsifier used, provided emulsions are compared under strictly identical conditions, seven-day old emulsions being compared.

Furthermore, as in figure 8, for 0.10 *M* sodium oleate concentration, the younger emulsion A′ has its maximum level at a higher per cent of small droplets than the older emulsion C′, but for 0.05 *M* sodium oleate concentration, B′ lies below A′. The first case is the reverse of what takes place in the case of octane emulsions. Perhaps when a high concentration of the emulsifier is used with a viscous oil the equilibrium is established in a different manner, owing to the difference in diffusion, and the influence of hydrolysis does not change it with time. The low concentration of the emulsifier 0.005 *M* sodium oleate in the stanolax oil emulsions indicates a behavior similar to that in the case of octane emulsions.

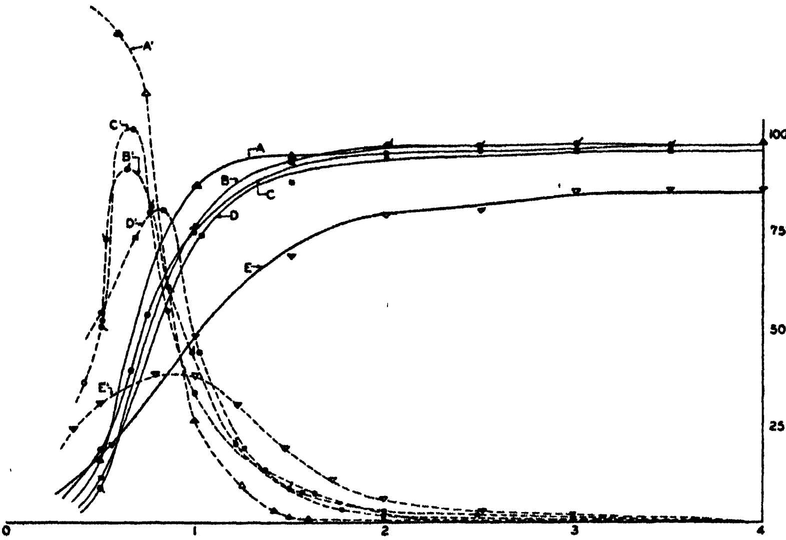

FIG. 9. STANOLAX-WATER EMULSIONS

△, AA′, 0.05 *M* sodium oleate, twelve days old; ρ, BB′, 0.05 *M* sodium oleate, seven days old; ○, CC′, 0.10 *M* sodium oleate, seven days old; ■, DD′, 0.005 *M* sodium oleate, four days old; ▽, EE′, 0.005 *M* sodium oleate, twelve days old.

CONCLUSIONS

A statistical method, using a microprojection equipment, was employed to obtain the number distribution curves for octane-water and stanolax-water emulsions with sodium oleate as the emulsifier.

The influence of various factors, such as concentration of the emulsifier, age of the emulsion, and presence or absence of hydrolysis in the systems concerned with reference to the distribution of sizes in both kinds of emulsion systems, was studied. From the experimental data, integral distribution curves were drawn. The results could only be interpreted by deriving mathematically the differential curves for the corresponding integral curves.

The shape and the level of the per cent of maximum small size globules on the derivative curves reflects the presence or absence of hydrolysis, high or low concentration of the emulsifier, and actual age of the emulsion. This method was proposed for measuring the stability of emulsions, and the latter was proved for the first time in the literature for stable emulsions four to five years old.

I desire to express my deep appreciation and most sincere thanks to Professor W. D. Harkins for his valuable suggestions and kind coöperation in this work.

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PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. VI

SOME APPLICATIONS AND LIMITATIONS OF THE SPECIFIC HEAT METHOD AS A "NON-COMPARATIVE CRITERION OF PURITY"

EVALD L. SKAU[1]

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Part III (8) of this series of papers contains a discussion of the enormous rise in the values of heat content and specific heat of a solid at constant pressure, $(\Delta H)_s$ and $(Cp)_s$, respectively, just below its melting (freezing) point owing to the presence of impurity. In Part V (9) it was pointed out that only a small amount of impurity is necessary to raise the value of $(Cp)_s$ above that of $(Cp)_l$, the specific heat of the liquid, at the freezing point, and it was shown that if $(Cp)_s > (Cp)_l$, we may at once suspect the presence of impurity in the sample. The purpose of the present communication is to point out certain possibilities which must be kept in mind in applying such heat content and specific heat data as a "non-comparative (10) criterion of purity."

Although there is a high probability that a given compound is quite pure if the value of $(Cp)_s$ increases almost linearly with temperature and so as not to exceed that of $(Cp)_l$ at the freezing point, actual exceptions and apparent exceptions exist. The actual exceptions comprise all the cases of impure samples where the change from the liquid to the solid state takes place completely at constant temperature, e.g., a eutectic mixture. The apparent exceptions are comprised of cases in which the change from the liquid to the solid state takes place over a temperature range but where this temperature range lies completely above the highest temperature for which the data for the heat content, and therefore for the specific heat, of the solid have been determined experimentally. This can best be seen by reference to a diagram.

In figure 1 the dotted lines and the upper full line represent the heat contents in calories per gram, ΔH, of pure benzene in the liquid and solid states

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at various temperatures near the freezing point, 5.5°C.; ΔH for the pure liquid at 5.5°C. is taken as zero. The full lines represent the heat contents of a 1-g. sample of benzene containing 1.48 mole per cent of naphthalene, i.e., enough to lower its freezing point 1°C. (See paper III of this series, samples I and V, respectively.) The eutectic temperature of this binary system is −3.5°C., i.e., 8°C. below the freezing point of the sample being considered, and the eutectic composition is about 13 mole per cent, 19.7 weight per cent, of naphthalene (12). The total heat change for 1 g. of the impure sample during its complete solidification can be calculated on

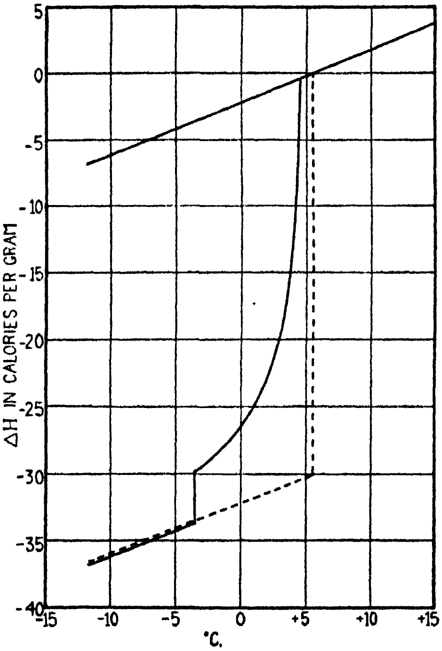

FIG. 1. HEAT CONTENT–TEMPERATURE CURVE FOR A PURE AND FOR AN IMPURE SAMPLE OF BENZENE

the basis of Washburn and Read's values and on their conclusion that the system behaves ideally. One gram of eutectic liquid would give up about $(0.197 \times 36.4 + 0.803 \times 30.1)$ or 31.35 calories during solidification, that is, about 1.25 calories per gram more than pure benzene. For the particular sample in question the amount of benzene crystals which would separate on cooling to −3.5° is 0.88 g. per gram of sample (8), so that there remains 0.12 g. of eutectic solution. This gives up 0.12×1.25 or about 0.15 calorie per gram more on solidification than the same amount of pure benzene. Thus it is obvious that the heat content of the sample completely solidified at the eutectic temperature is 0.15 calorie per gram lower than that for benzene. This is represented in figure 1 by the sharp drop in the heat content curve at −3.5°.[2] Below this temperature the curve would be expected to run practically parallel to that for pure benzene since the slope, i.e., the specific heat, will not be much different, the specific heat of crystalline mixtures being an additive property (7). The uppermost curve in figure 1, i.e., that for the liquid and supercooled liquid states, can be considered as the same for the pure and slightly impure benzene.

From figure 1 it is obvious that if the heat data for the impure sample in question did not include any values for the temperature range −3.5° to +4.5°C., the data would be interpreted as proving that the sample was highly pure, since the specific heat of the solid would be almost linear with respect to the temperature and apparently $(Cp)_s < (Cp)_l$ at the melting point. This would also be true in case the benzene contained any concentration of naphthalene as impurity up to 20 per cent by weight and indeed, since the same condition would exist on the other side of the eutectic, it would be impossible to distinguish by means of this heat data alone between a pure compound and a sample containing as high as 30 to 40 weight per cent of naphthalene.

The case of cerotic acid reported by Garner and King (4) probably falls in this category. These authors pointed out that although the sample was a mixture of at least two acids, probably $C_{26}H_{52}O_2$ and $C_{28}H_{56}O_2$, as shown by x-ray analysis (3), the curves for the specific heat up to within 6°C. of the freezing point failed to show the usual abnormalities indicative of the presence of impurities. It seems probable therefore that the eutectic temperature for the mixture falls within 6°C. of the freezing point. Indeed this is in accord with the fact that an equimolecular mixture of the straight chain acids $C_nH_{2n}O_2$ and $C_{n+2}H_{2n+4}O_2$ has a melting point only 6.1°C. below the freezing point of the C_n acid when $n = 16$; 5.5°C. when $n = 18$; 4.4°C. when $n = 20$; 4.3°C. when $n = 22$; and 4.2°C. when $n = 24$ (3). For the mixture of the C_{26} and C_{28} acids, therefore, the melting point would be expected to be about 4°C. below the freezing point of the C_{26} acid.[3]

Let us finally point out a possible misinterpretation of the heat content and specific heat data when the data for the range just below the melting point are complete. *The curve for the sample of benzene containing 1.48 mole per cent of naphthalene as impurity, given in figure 1, might be mistaken for that for a nearly pure compound with a transition point at −3.5°C., the*

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[2] In actual practice this drop does not take place at a constant temperature since, as in the case of the pure substance, even a trace of impurity causes the solidification to take place over a range.

[3] The fact that the heat of fusion for this sample as obtained by Garner and King (4) is much lower than that of either the pure C_{26} or C_{28} acid, indicates, if we assume that the sample contained no other impurity, that this binary system is not ideal.

β-form being stable below that temperature and the α-form above.[4] It is therefore at once obvious that such a heat content curve with a break below the melting point cannot safely be accepted as definite proof of a transition point unless the curve just below the *melting* point (instead of below the supposed transition point) indicates that the sample is highly pure.

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[4] The heat of fusion of the α-form would then be taken as the difference in the heat content of the liquid at +4.5°C. and that of the "solid form" obtained by extrapolating the curve for the solid from just above −3.5°C. up to +4.5°C. The heat of transition would be taken as the difference between the heat content of the "solid α" and the "solid β" at +4.5°C. by extrapolation of the corresponding curves up to +4.5°C.

THE DROP-WEIGHT METHOD FOR THE DETERMINATION OF ELECTROCAPILLARY CURVES

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Electrocapillary curves for non-aqueous solutions are of interest in assessing the rôle of the solvent in the double layer at a metal–solution interphase, but in an attempt to extend previous electrocapillary work to such solutions, it was found that the accuracy of a capillary electrometer was very much diminished, since the liquid no longer wets the glass perfectly and the angle of contact between the mercury and the glass is less than 180° by an uncertain and variable amount. In bad cases it is impossible to determine an electrocapillary curve at all in this way. It is therefore a matter of importance to examine other methods for the determination of electrocapillary curves, methods that may not suffer from this defect, and can be used to obtain electrocapillary data for non-aqueous solutions.

The drop-weight method was first used by Kučera (4) and has since been employed in electrocapillary work for special purposes in a limited number of cases, but only the following facts regarding its applicability and accuracy have emerged. (a) Kučera found that, if throughout the course of an electrocapillary curve, the dropping rate is kept constant and slow, the drop-weight–potential curve is roughly parallel to the corresponding electrocapillary curve. The only data for electrocapillary curves available at that time were those of Paschen (5), so that, by modern standards of accuracy, this rough agreement is not very significant. (b) In dilute aerated solutions a spurious maximum occurs on the positive branch of the drop-weight–potential curve, owing to the reduction of the oxygen present in the solution (Heyrovský (3)), but this can be avoided by using air-free solutions. In any case the effect only becomes large if the solution is very dilute. (c) When the interphase between the mercury and the solution is non-polarizable, the drop-weight method is particularly liable to lead to false results, but this is now well understood (see Craxford (2)) and need not be discussed here, since this paper is concerned only with the polarized interphase.

Thus before confidence can be placed in electrocapillary curves obtained by the drop-weight method, it is necessary to develop a reliable drop-weight technique for electrocapillary problems, and to compare curves obtained by it with the corresponding curves obtained by the use of an accurate capillary electrometer. Such a comparison is necessary, since a detailed application of the mathematical theory of the drop-weight method is impracticable, and it is therefore unjustifiable to assume, without experimental proof, that the surface tension is linearly proportional to the drop-weight over the whole of the electrocapillary curve. The requisite experimental proof of this assumption is given in this paper.

EXPERIMENTAL DETAILS

Two forms of apparatus were used for the determination of drop-weight electrocapillary curves under air-free conditions, and they are sufficiently described by the diagrams (figures 1 and 2). The construction of the capillary, at the tip of which the mercury drops are formed, is however a rather more subtle matter. Kučera drew out a piece of ordinary thermometer tubing, and broke it off cleanly under water. The radius of the tip, which was the narrowest part of the capillary, was of the order of 0.002 cm., but with this arrangement Kučera was unable to extend his electrocapillary curves to potentials appreciably more negative than the electrocapillary maximum, on account of active electrolysis. Preliminary trials with such capillaries gave rather uneven curves, probably due to small changes in the effective radius of the capillary tip, arising from the very slow but unavoidable electrolysis that always takes place when a mercury surface is polarized. Such changes would become unimportant if the capillary tip were larger, and this would also effect a considerable saving of time, because for each measurement, a large number, fifty to one hundred, of the very small drops have to be counted out in order that their total weight may be large enough to minimize errors in weighing. Using wider capillary tips, only relatively few, ten to twenty, drops need be collected and weighed together each time. Hence the method used by Bennewitz and Delijannis (1) was tested, because this involves a capillary with a radius of about 0.1 cm., which is constricted above the tip so as to reduce the rate of flow by the desired amount. This gives smooth and reproducible curves only at the more positive potentials, in fact, at those potentials used by Bennewitz and Delijannis. As the mercury becomes more negative, very small amounts of gas form high up in the capillary and collect in the constriction, so breaking the thread of mercury. This insulates the drop of mercury that happens to be forming at that time, and thereby alters its potential, and hence its surface tension. The gas bubble is then swept down by the flowing mercury into the wider parts of the capillary, where it disperses to the walls and rises up into the constriction once more. This cycle is repeated many times before the bubble becomes large enough to be finally swept out of the capillary. While these processes are occurring the drop-weight is clearly unreproducible and useless. This difficulty has however been eliminated by the type of capillary shown in the figures, where a large bulb, A, containing about 10 cc. of mercury, is interposed between the capillary tip and the constriction B. The top of the tube C is connected to a mercury reservoir by means of a rubber tube. This arrangement effectively prevents the collection of gas in the constriction, and its use enables electrocapillary curves to be prolonged almost

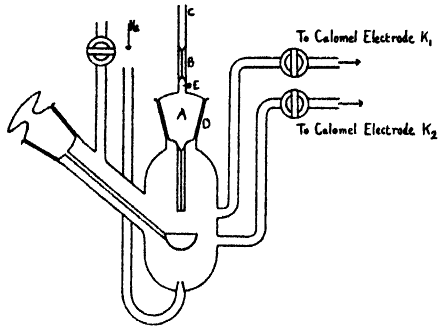

FIG. 1. APPARATUS USED FOR THE DETERMINATION OF DROP-WEIGHT ELECTROCAPILLARY CURVES

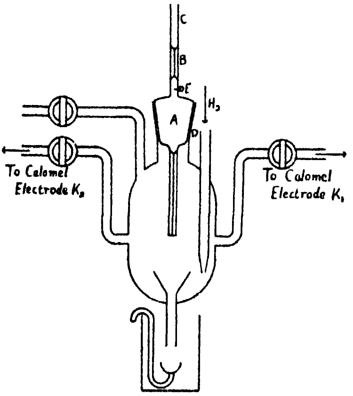

FIG. 2. APPARATUS USED FOR THE DETERMINATION OF DROP-WEIGHT ELECTROCAPILLARY CURVES

as far into the negative region of potential as with an ordinary capillary electrometer. The interposed bulb also prevents foreign bodies or other impurities derived from the rubber tube from reaching the capillary tip, and so vitiating the surface tension measurements, because in the course of each series of experiments the volume of mercury that drops through the capillary is considerably less than the volume contained in the bulb A.

For each series of measurements, the apparatus is thoroughly cleaned, filled with the necessary solution, a cork inserted at D instead of the capillary, and the air removed by bubbling oxygen-free hydrogen for several hours. Meanwhile the bulb A of the capillary is filled with pure mercury, and connected by means of a rubber tube to the mercury reservoir, taking care to enclose no air bubbles in the connection. The mercury used was purified and redistilled *in vacuo*, and the rubber tube was freed from sulfur compounds by boiling first in caustic soda solution, and then several times in distilled water. After being dried, it was shaken out several times with pure mercury before use. When mercury has begun to drop from the capillary, the latter is inserted into D in place of the cork, and after standing for half an hour for everything to come to a steady state, measurements may be commenced. The whole apparatus is fixed to a very heavy stand on a brick pillar, built in a basement laboratory, to avoid vibration, which Kučera showed to have a very large effect on the drop-weight. For each measurement the dropping mercury is polarized to the required amount by applying a suitable potential difference between the contact E and the polarizing electrode K_1, and hydrogen is bubbled through the solution for about ten minutes, and is then turned off. The potential of the dropping mercury is then measured against the calomel electrode K_2. The potential usually fluctuates slightly according to the state of the drop, but clearly, it is the value just before the drop breaks away and falls, that is connected with its surface tension. There is no difficulty in measuring this potential, but in any case the fluctuation is small. The height of the mercury reservoir is then adjusted until the dropping rate becomes equal to any desired value, which must be kept fixed for each series of measurements. This rate must be a slow one, of the order of one drop every six or more seconds. The collecting spoon is then moved under the capillary, and twenty drops counted out and removed. The potential is again measured. The drops are poured into a 5-cc. crucible, washed twice with distilled water, and dried with strips of filter paper. The crucible is then placed in a vacuum desiccator, and its contents weighed next day. If, after each series of measurements, the capillary is washed thoroughly, it will continue to give satisfactory results for a long period of time.

RESULTS

Table 1 contains the results of such measurements for *N* potassium nitrate solution. Column 2 contains the weights of twenty drops, and column 3 the surface tension for the same potential, measured by means of an accurate capillary electrometer. The ratio of the surface tension at the maximum to the maximum drop-weight is 305.1, and this factor is then used to convert each of the drop-weight values to surface tensions, by multiplication, and the result is given in column 4. The agreement between columns 3 and 4 throughout the whole of the range of potential employed shows that the drop-weight method is accurately applicable to the determination of electrocapillary curves. At any potential the surface tension, as given by this method, is always well within 1 dyne per centimeter of the value given by the capillary electrometer, and hence the surface tension is correct to within 0.2 per cent.

TABLE 1

The electrocapillary curve for N potassium nitrate at 15°C.

POTENTIAL (N. CAL.)	DROP-WEIGHT (20 DROPS)	SURFACE TENSION MEASURED BY CAPILLARY ELECTROMETER	SURFACE TENSION CALCULATED FROM DROP-WEIGHT
	grams	*dynes per cm.*	*dynes per cm.*
−0.011	1.2390	378.3	377.9
−0.046	1.2548	382.2	382.7
−0.073	1.2673	386.8	386.7
−0.145	1.2956	395.7	395.3
−0.178	1.3077	399.2	398.8
−0.211	1.3185	402.6	402.3
−0.247	1.3306	406.0	406.0
−0.286	1.3430	409.3	409.8
−0.326	1.3530	412.3	412.8
−0.361	1.3611	414.8	415.2
−0.392	1.3667	416.4	417.0
−0.433	1.3732	418.5	419.0
−0.470	1.3764	419.8	420.0
−0.516	1.3791	420.8	420.7
−0.545	1.3807	421.2	421.2
−0.578	1.3810	421.3	421.3
−0.613	1.3803	420.9	421.1
−0.649	1.3789	420.2	420.7
−0.679	1.3752	419.2	419.6
−0.714	1.3710	417.6	418.2
−0.760	1.3625	415.2	415.7
−0.816	1.3504	411.7	411.9
−0.863	1.3388	407.9	408.4
−0.907	1.3257	404.0	404.3
−0.959	1.3093	399.2	399.3
−1.008	1.2928	394.0	394.4
−1.048	1.2736	389.4	388.6
−1.107	1.2529	382.3	382.2
−1.167	1.2288	374.4	374.8

SUMMARY

A technique for the determination of electrocapillary curves by the drop-weight method has been developed, and the resulting curves are shown to coincide to within 0.2 per cent with the corresponding curves obtained in the usual way with a capillary electrometer.

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THE PHYSICAL CHEMISTRY OF FLOTATION. V

FLOTATION OF GRAPHITE AND SULFUR BY COLLECTORS OF THE XANTHATE TYPE AND ITS BEARING ON THE THEORY OF ADSORPTION

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Gaudin (3) states that graphite and sulfur are intensely water-repellent and that to float them it is often sufficient to add a "frother" such as pine oil. Though other oils are sometimes added, Gaudin does not attribute their beneficial effect to their functioning as collectors. Nor does he attribute any collecting power to the frothers, but assumes that the natural floatability of these two minerals is sufficient to account for their flotation. Xanthates, it is claimed, exercise no collecting function toward sulfur and graphite, and their addition would be merely wasteful.

We have found, however, that concentrations of frothers considerably in excess of those required to produce a good froth are necessary to induce good flotation of graphite. With certain other frothers in neutral solutions, no substantial flotation is obtained whatever their concentration, and it has been concluded that graphite, like most other minerals, requires a collector for satisfactory flotation. In those cases where a reagent, usually regarded purely as a frother, is alone sufficient to induce good flotation, it has been shown that the reagent is itself a collector for the graphite. Contrary to the generally accepted view, it has been found that collectors of the xanthate type (xanthates, dithiocarbamates, dithiophosphates, etc.) are excellent collectors for both graphite and sulfur. Sulfur occupies a different position from graphite since it usually floats readily without any collector. Under some conditions, however, the floatability is considerably enhanced by collectors of the xanthate type, and it has been shown, moreover, that they are abstracted from solution by the sulfur.[1]

The response of graphite and sulfur to collectors of the xanthate type is of considerable theoretical significance. It does not seem possible to connect the response of a mineral with the possession of any particular type of lattice structure by the mineral. Sulfur and cleiophane, cerussite and anglesite, graphite, galena and chalcopyrite, copper and gold represent among them several different types of crystal lattice, but they all adsorb xanthates from solution, and, what is more significant, all lead to the same maximum angle of contact for each xanthate at a line of triple contact air–solid–xanthate solution. The last-mentioned fact indicates that, following the adsorption of the xanthate, the external or effective surface is the same in all cases, and that it consists entirely of the non-polar groups of the orientated adsorbed xanthate molecules.

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[1] In an earlier paper (6) we made the statement that sulfur is not influenced by xanthates. This incorrect view was due to our not having experimented with sufficiently high concentrations of ethyl xanthate.

It would be premature to conclude that the nature of the forces binding the xanthate molecules to these vastly different surfaces is the same for all of them. Nevertheless there emerges from these observations sufficient evidence to prove that certain of the proposed theories of adsorption cannot be of general application.

Taggart (5) claims that chemical (soluble) collectors function by forming a substantially insoluble orientated water-repellent film on the surface of the mineral to be floated. He has endeavored to show that this film is formed by double decomposition between the soluble collector and the surface of the mineral. In cases where the solubility of the mineral is so low as to render such action improbable, as, for example, galena, it is assumed that a previous oxidation has already changed the mineral surface into some compound of suitable solubility. Though it has been shown that the surface of galena may become oxidized and that the oxidized film may react with ethyl xanthate by double decomposition, it has not, in our opinion, been shown that unchanged galena cannot adsorb ethyl xanthate. Indeed, the procedure for floating anglesite in practice, namely, to add sodium sulfide as well as xanthate, points to the conclusion that lead sulfide itself adsorbs ethyl xanthate more readily than does lead sulfate. This may be demonstrated by air–mineral contact tests, as will be shown in a future publication.

At the surfaces of sulfur and graphite there can be no chemical reaction with xanthate of the type postulated by Taggart. The double decomposition theory cannot therefore be of general application, even if it be true in certain cases. The constancy of the contact angle, whatever the adsorbing solid, suggests, however, that the forces causing adsorption of xanthates are similar for all solids, and that any theory of the action of xanthates should explain their action on graphite as well as on galena.

While it is contended that the simple chemical theory of adsorption should logically be abandoned, certain observations that lent support to it should not be forgotten, though the reason for them is obscure. The readiness with which a sulfide mineral adsorbs a collector of the xanthate type increases as the solubility of the compound formed between the base metal of the mineral and the collector decreases. It should be pointed out however, that since the solubilities of the heavy metal xanthates run strictly parallel with the solubilities of their sulfides, this generalization might be expressed in an alternative form, namely, that the readiness with which a sulfide mineral adsorbs a collector of the xanthate type increases as the solubility of the mineral decreases.

It is dissatisfying to reject one theory of adsorption without substituting for it another theory that is in agreement with experimental facts. It is therefore proposed to consider the nature of the forces at the surfaces of solids with a view to deciding whether sufficient is known concerning them to provide an explanation for the adsorption of collectors. It is generally agreed that surrounding each of the atoms or ions of a solid there exist strong forces which are responsible for the cohesion that opposes cleavage or grinding, and which lead to high melting and vaporization temperatures. At the surface these forces are available for attracting other ions, atoms, or groups of atoms, but until recently very little was known of their magnitude. De Boer and Custers (2) have, however, made an attempt to calculate the energy of adsorption of phenol on sodium chloride, dividing the binding forces into two types, the van der Waals forces and the electrostatic forces. It was shown by them that molecules with a high dipole moment are preëminently adsorbed electrostatically by the ions of the crystal lattice, whereas the van der Waals forces are operative for the nonpolar portion of the adsorbed molecules. The soluble flotation reagents known as collectors possess either a high dipole moment or a high degree of dissociation. Most of the adsorption of common collectors on solids possessing an ionic lattice structure must therefore be attributed to electrostatic forces emanating from the surface ions, acting either on the dipoles or the dissociated ions of the collector.

For solids of the graphite type, in which the electrons are shared equally between the atoms of the crystal lattice, different considerations must apply, and in this case it is difficult to reconcile the interior structure with an apparently undiminished ability to adsorb the xanthate type of collector. At the surface of such solids there must be a different arrangement of the electrons and a development of more polar characteristics.[2] The structure of graphite is such that the surface consists of a hexagonal pattern of carbon atoms with alternate carbon atoms having available one electron for sharing with any atom or group also capable of supplying an unshared electron. Before it can adsorb xanthate or during the adsorption, a rearrangement of electrons is necessary. Of the carbon atoms carrying an unshared electron every second one would be able (if spatial considerations permitted) to adsorb a xanthate ion, while the other similar atoms would accept the electron available from these atoms on which adsorption occurs.

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[2] Adams and Jessup (1) have shown by means of contact angle measurements on original crystalline surfaces and on surfaces produced by scraping, that the surface forces differ according to the method of producing the surface. Surface rearrangements are therefore sometimes necessary for thermodynamic equilibrium, but the rate of rearrangement may be infinitesimally small.

It has been found that the adsorption of ethyl xanthate by graphite does not change the pH value of the solution; it follows that xanthic acid[3] alone is not adsorbed, for if it were, the solution would develop alkalinity. It has been shown, too, that the xanthate adsorbed on graphite may be approximately determined by an iodine titration; it cannot therefore be present as dixanthogen. Since xanthic acid is a strong acid, it is probable that undissociated potassium xanthate is not adsorbed. We are therefore led independently to the conclusion that the xanthate ion is adsorbed. Graphite can supply no ion to replace the xanthate ions adsorbed, and unless a positive ion (potassium ion) is also adsorbed, the graphite must become strongly negatively charged following the adsorption. There probably exists a surrounding layer of potassium ions.

It is well to consider the difference between this conception of the adsorption of xanthate ions and Taggart's conception of chemical action, since the external appearance of the solid with its adsorption film is identical according to the two theories. Nothing is known of the crystal structure of lead xanthate, but it must certainly be very different from that of lead sulfide. The interior forces of the lead xanthate lattice must differ from those of the lead sulfide lattice, and the surface forces also must differ. These differences are manifested in the different solubilities in water and alcohol, and in the great ease with which air displaces water at the surface of the former. Consequently, the forces available to bind a xanthate ion to the surface of lead sulfide (by adsorption) must differ from those available to bind the same ion to the surface of lead xanthate (by crystal growth). The concentration of xanthate ions in equilibrium with two such different surfaces must therefore differ. Hence, in an earlier paper (4) Taggart was led to express tentatively the view that "the solubility of the substance as a surface coating is somewhat less than that of the same substance independently put into solution." This statement must be interpreted as meaning that lead sulfide binds a xanthate ion to its surface more firmly than does lead xanthate. We have found it useful to retain the conception of an "adsorption solubility product" of lead xanthate at such a surface. Provided that it is not confused with the true solubility product of lead xanthate, there can be no confusion due to its use. It is merely implied that the concentration of the lead ion in solution influences the adsorption of xanthate ions at a lead sulfide surface in a manner qualitatively similar to but differing quantitatively from the manner in which it is known to influence the deposition of sulfide ions at the surface.

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[3] Barsky (7) has suggested that xanthic acid may be adsorbed by galena.

Taggart's suggestion that there must first be formed a film of sulfate (or other sulfoxide) before adsorption can occur, leads to an alternative picture, with an intermediate layer of lead sulfate between the lead sulfide and the xanthate film. (If this intermediate film be not retained in the final model, the supposed conversion to sulfate loses its significance. For if a xanthate ion *can* ultimately be attached to the sulfide lattice it is clearly unnecessary to postulate a sulfate layer at any stage of the process.) Here again the forces binding the xanthate ion to the surface differ from those binding it to a lead xanthate lattice, and the surface cannot be identical with a surface of pure lead xanthate.

EXPERIMENTAL METHODS

A. Contact angle measurements

These have been carried out by the methods described in the third paper of this series (8). The sulfur specimens were cut from a solid obtained by allowing fused flowers of sulfur to cool. The usual methods of polishing are satisfactory for sulfur, but not for graphite. None of the methods tried gave a polish as good as can be obtained on specimens of the sulfide minerals or metals, and the use of linen as a final polishing medium was useless. Magnesium oxide as abrasive on a plane lead or aluminum plate proved moderately satisfactory.

B. Flotation tests

Grinding was accomplished under water with a porcelain pestle and mortar, and the pulp was deslimed by shaking with water in the test tube and pouring off the mineral that did not settle within fifteen seconds. The flotation tests were carried out in rubber stoppered test tubes (size 6 in. x 1 in). About 2 g. of ground material with 30 cc. of water were introduced and the reagents added. The tube was then shaken vigorously. If a frother is present an excellent froth can be produced in this way, and if the mineral is in a condition susceptible to flotation from 50 per cent to 100 per cent of it will float in a well-mineralized froth that does not collapse on standing. Even when the mineral is not in a condition susceptible to flotation, a few particles usually float in an incomplete film on the surface. Unless the particles in the surface showed crowding this small tendency to float was ignored. Though the method is incapable of giving results that could be applied without modification in practice, it is a more rapid and more easily controlled medium for studying the effects of reagents than an ordinary flotation machine. The major differences between the test tube and the flotation machine lie in the method of aeration, and in the pulp density.

C. Consumption of xanthate

The xanthate was estimated before and after the abstraction tests by titration against standard iodine. The precautions necessary because of the low concentrations of xanthate and the consequent use of *N*/1000 iodine will be described elsewhere.

EXPERIMENTAL RESULTS

Graphite

Flotation in the absence of reagents. Ground graphite will float in an incomplete film if it is fed carefully on to the surface of water. If, however, it be once submerged, only a small proportion of the particles will float again. Washing with ether, to remove any adherent oil, has little effect on the flotation of graphite, nor does heating to a red heat, with or without subsequent quenching in water. It does not seem to matter whether the graphite is ground dry or under water.

Effect of the recognized frothers. Under the conditions of these test tube tests, 10 mg. of terpineol (one of the major constituents of pine oil) per liter gives a fairly stable froth in water, but between 25 and 50 mg. of terpineol per liter is required to produce satisfactory flotation of graphite. With isoamyl alcohol 30 mg. per liter gives a fairly stable froth in water, but between 200 and 500 mg. per liter is required to produce a good flotation of graphite. Neither of these frothers induces satisfactory contact in contact angle tests, though solutions of high concentration lead to slight and irregular contact.

Acetone, though a frother, is not, in neutral solution, a collector for graphite. One gram of acetone per liter gives a froth of low stability, and with 200 g. per liter the froth is still not very stable. Whatever its concentration, however, acetone is without influence on the floatability of graphite. If a suitable collector is present as well (e.g., 5 mg. of potassium amyl xanthate per liter), the acetone exerts the usual function of a frother in facilitating the formation of a stable mineralized froth; about 10 g. per liter is necessary for this purpose. Ethyl alcohol and cyclohexanol are frothers that behave in a manner similar to acetone.

In alkaline solutions all of these frothers give stable froths at lower concentration and all of them lead to flotation of graphite. Whereas in the absence of a collector 2 g. of acetone per liter gives appreciable flotation at pH = 12, and 10 g. per liter gives good flotation, in the presence of 10 mg. per liter of potassium amyl xanthate 250 to 500 mg. per liter of acetone gives good flotation. In general it has been found that the addition of amyl xanthate permits of the flotation (especially of the larger particles) with considerably lower concentrations of "frother" than would otherwise be possible, and this is true whether alkaline or neutral solutions are used.

Effect of collectors of the xanthate type. Ethyl xanthate, if at sufficiently high concentration, is a good collector for graphite in test tube flotation tests. In these tests isoamyl alcohol (30 mg. per liter) was used as the frother. About 25 mg. of ethyl xanthate per liter definitely gives some flotation, but higher concentrations are required to give a permanent mineralized froth. Contact angles varied from approximately 30° for a concentration of 5 mg. per liter to 60° for concentrations greater than 200 mg. per liter. Copper sulfate did not improve either contact or flotation at the lower concentrations of xanthate; it is not an activating agent for graphite.

A concentration of 5 mg. of potassium amyl xanthate per liter gives good flotation of graphite; again 30 mg. of isoamyl alcohol per liter was used as frother. Contact angles varied from 57° for a concentration of 5 mg. per liter of potassium amyl xanthate to 80° for a concentration of 500 mg. per liter. Cyanide (1 g. of sodium cyanide per liter) is without influence on flotation or on contact, but after a short conditioning period strong alkali (pH = 13) prevents flotation, probably because it slowly saponifies the xanthate. If a solution containing 5 mg. of potassium amyl xanthate per liter is kept at pH = 13 for an hour before use, it fails to induce flotation of graphite.

Of the dithiocarbamates the butyl compound is more effective than the ethyl. Potassium dibutyl dithiocarbamate (10 mg. per liter), with isoamyl alcohol (30 mg. per liter) as frother, induces excellent flotation of graphite. Solutions containing 5, 50, and 500 mg. per liter induced contact angles of 58°, 65°, and 74°, respectively. Sodium diethyl dithiophosphate must be at a high concentration to cause flotation. As the concentration is increased, flotation first becomes possible at about 500 mg. per liter, but 10 g. per liter gives excellent flotation. The latter concentration leads to a contact angle of 60°.

Thus, graphite generally responds to collectors of the xanthate type (containing the CS_2 group) in the same order as the sulfide minerals, which are least susceptible to the dithiophosphates, most susceptible to the dithiocarbamates, and of intermediate susceptibility to the xanthates. Like those on sulfide minerals, the collector films on graphite are very stable. Amyl xanthate cannot be recovered from the surface by washing with hot water or alcohol.

Consumption of xanthate. Graphite rapidly abstracts ethyl xanthate and amyl xanthate from their solutions. Within ten minutes 2 g. of dry ground graphite completely removed the amyl xanthate from 20 cc. of a 20 mg. per liter solution. Within half an hour 2 g. removed 69 per cent of the amyl xanthate from 40 cc. of a 500 mg. per liter solution, and 50 per cent from a second similar solution. The pH value remained unchanged at 6.8; had xanthic acid been abstracted the pH value would have changed to between 10 and 11. Similar results were obtained for ethyl xanthate.

It is impossible to recover the adsorbed xanthate by digestion of the graphite with hot water or hot alcohol. That the xanthate has been adsorbed unchanged on the surface of graphite is, however, suggested by the results of a titration of a suspension of the conditioned graphite against $N/1000$ iodine. The reaction is a slow one, several hours' contact with the iodine solution being necessary, and an accurate titration is impossible. However, at least 80 per cent of the adsorbed ethyl xanthate can be evaluated in this way. In a control test, graphite that had not been treated with xanthate consumed less iodine than corresponds to 10 per cent of this amount.

Sulfur

Sulfur differs from graphite in that it is inherently much more readily floatable. Sulfur that has been ground very coarsely under water does not float completely on shaking it up with water or dilute solutions of the frothers already mentioned, but if it be allowed to slide slowly on to the surface a heavy film flotation can usually be obtained. However, by using coarse sulfur and low concentrations of frothers, it can be demonstrated that the xanthate type of collector, if present in sufficiently high concentration, enhances the floatability of sulfur. The adsorption of the collector by sulfur may also be studied by measuring the contact angle at its surface in the presence of a solution of the collector. Thus 500 mg. of potassium di-*n*-butyl dithiocarbamate per liter led to an angle of contact of 78°. Amyl xanthate did not, however, induce the customary angle of contact.

TABLE 1

Abstraction of amyl xanthate by two grams of sulfur

NO.	CONCENTRATION OF XANTHATE		IODINE EQUIVALENT OF XANTHATE ABSTRACTED	XANTHATE ABSTRACTED
	Initial	Final		
	mg. per liter	*mg. per liter*	*cc.*	*mg.*
1	312	268	3.4	0.70
2	156	108	3.7	0.77
3	94	50	3.4	0.70
4	31	0	2.5	>0.5

We cannot confirm a statement by Christmann (7) that whereas sulfur is not wetted by water, pine oil causes it to be readily wetted by water. We find that the floatability of sulfur is considerably increased by the addition of pine oil. If sufficient pine oil is added to give large undissolved globules, the sulfur, being wetted by pine oil in preference to water, goes into the pine oil phase, or into the interface. The combined sulfur-pine oil aggregate is readily wetted by air and floats readily, unless sufficient sulfur is present to make its density greater than that of water. Christmann's conclusion that the polar group of the pine oil is orientated outwards at the surface of sulfur is therefore unjustified.

The adsorption of collectors by finely divided sulfur has been determined by measuring the abstraction of xanthate from solution. Table 1 demonstrates that the amount of amyl xanthate removed is independent of the initial concentration of the xanthate, and that the whole of the xanthate may be removed from sufficiently dilute solutions. Two grams of flowers of sulphur and 16 cc. of xanthate solution were used for each test, three hours' contact being allowed between sulfur and solution. The sulfur was then washed until the washings were free from xanthate and the unconsumed xanthate determined by titration against $N/1000$ iodine. In order that the sulfur should be wetted by the xanthate solution, it was first wetted by 1 cc. of acetone. In a control test without sulfur, but with acetone, there was no appreciable loss of xanthate.

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THE EFFECT OF ELECTROLYTES UPON THE RATE OF HYDROLYSIS OF DIETHYL ACETAL[1,2]

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The kinetic method for the determination of the dissociation constant of benzoic acid in potassium chloride solutions has been shown to yield results in agreement with the electrometric method (7, 10).

In order to determine the dissociation constants of acids in solutions of other salts, it is necessary to calibrate the reaction for these salt solutions. This involves a study of the primary kinetic salt effect of the reaction. The present paper extends the study of Kilpatrick and Chase to eight solvent salts. The results are not only of value for the determination of hydrogen-ion concentrations, but in themselves they are of interest as a study of primary kinetic salt effect in a reaction of the zero kinetic type, $A^0 + B^- \rightarrow$ products.

The rate-determining step may be regarded as the formation of the complex as postulated by Brönsted (2, 3) or the decomposition of the intermediate complex in equilibrium with the reactants (1). In either case the equation which expresses the kinetic salt effect for this type of reaction is

$$\ln k_{H_3O^+} = \ln k^0_{H_3O^+} + (\beta + \beta' - \beta'')C \tag{1}$$

where $k_{H_3O^+}$ represents the velocity constant for molar hydrogen ion at the concentration C of the uni-univalent salt, and $k^0_{H_3O^+}$ is the velocity constant for molar hydrogen ion at zero electrolyte concentration. β is the salting-out constant for acetal in the equation,

$$\ln f_0 = \beta C \tag{2}$$

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[1] An abstract of this paper was presented at the Eighty-sixth Meeting of the American Chemical Society, held at Chicago, Illinois, September, 1933.

[2] Abstracted from the dissertation of Leonard C. Riesch which was presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[3] George Lieb Harrison Fellow in Chemistry, 1933–1934.

and β' and β'' are the salting-out terms for the ions in the expression,

$$\ln f = -\alpha\sqrt{C} + \beta' \text{ (or } \beta''\text{)} C \qquad (3)$$

where β, β', and β'' depend upon the specific electrolyte.

Equation 2 has been shown to hold over wide ranges of concentration in certain cases (11). Equation 3 would not be expected to hold over a wide range of concentration.

An examination of the results in the literature indicates that the magnitude of the electrolyte effect varies greatly. Two typical examples are given in figure 1, in which $\frac{\log k_{H_3O^+} - \log k^0_{H_3O^+}}{C}$ is plotted against the electrolyte concentration C.

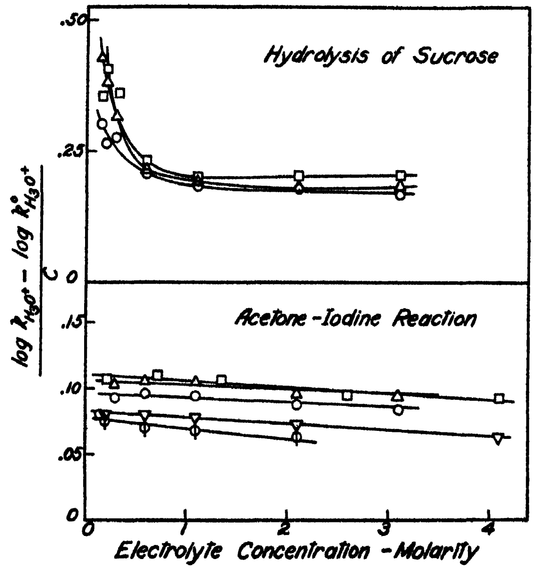

FIG. 1. THE VARIATION OF THE B VALUES WITH ELECTROLYTE CONCENTRATION
○, KCl; △, NaCl; □, LiCl; Φ, KNO_3; ▽, $NaNO_3$

The points represent the values of B, which equals 2.3 ($\beta + \beta' - \beta''$), at the various concentrations. It is to be noted that in the case of the acetone–iodine reaction B is small and fairly constant, while in the case of the hydrolysis of sucrose B decreases until an electrolyte concentration of approximately one molar is reached, after which B remains almost constant.

For small values of B and low concentrations, equation 1 reduces to the form,

$$k_{H_3O^+} = k^0_{H_3O^+} + \lambda C \qquad (4)$$

This equation has been subjected to many experimental tests in dilute solution and has been shown to hold within the accuracy of the measurements (4).

In the case of diethyl acetal the B value is large, and equation 4 cannot be expected to hold, but through the range of concentration where equation 3 is valid, log $k_{H_3O^+}$ should be a linear function of the concentration. A few experiments reported by Brönsted and Wynne-Jones (6) apparently show this to be the case.

Brönsted and Grove (5) have studied the primary salt effect in the hydrolysis of dimethyl acetal, and find that while the magnitude of the effect depends upon the particular electrolyte, equation 1 holds up to a concentration of 0.2 molar. The results reported herein indicate that equation 1 does not hold very exactly even in dilute solutions, but that B becomes fairly constant at high concentrations.

EXPERIMENTAL PART

The course of the reaction was followed dilatometrically, the apparatus and the method of calculation being the same as that used by Kilpatrick and Chase (10).

The acetal was purified by fractional distillation after treatment with anhydrous potassium carbonate, the fraction boiling between 102.5–103°C. (760 mm.) being used. It was essential that the acetal be free from acidic impurities. Frequent tests for acidic impurities were made by adding 0.5 cc. of acetal to 50 cc. of carbon dioxide-free water containing bromothymol blue. During the course of the work it was found necessary to keep the acetal in tightly stoppered bottles to prevent the formation of acetic acid. Apparently a trace of moisture and acid result in the hydrolysis of the acetal to acetaldehyde, which on oxidation yields acetic acid thereby increasing the amount of acid present and the rate of hydrolysis. The salts were purified when necessary. The sulfonates were recrystallized several times from alcohol after decolorization with activated charcoal.

An inspection of table 1 indicates that there is apparently a slight increase in $k_{H_3O^+}$ with increasing concentration, and a difference between the acids; however, this is probably within the experimental error of the measurements. We have therefore taken $k^0_{H_3O^+}$ as 2.469.

Table 2 gives the results with lithium chloride solutions. The magnitude of the electrolyte effect is thirteen-fold at three molar, and even at 0.2 molar it is 27 per cent. Table 3 summarizes the $k_{H_3O^+}$ values for the other salts. The specific effect of the various salts is evident. The $k_{H_3O^+}$ values vary over 100 per cent at some concentrations. Table 4 gives the B values calculated as for figure 1. From this table it is evident that the B values are much greater than those given in figure 1 for other reactions,

TABLE 1

Results at low electrolyte concentration

ACID	CONCENTRATION	k (OBSERVED)	$k/C_{\text{acid}} = k_{H_3O^+}$
	moles per liter		
HCl	0.00502	0.01221	2.432
HCl	0.010096	0.02478	2.454
HCl	0.01004	0.02456	2.445
HCl	0.01004	0.02447	2.439
HCl	0.01506	0.03736	2.480
HCl	0.02008	0.05021	2.501
HNO_3	0.00510	0.01244	2.439
	0.01020	0.02507	2.458
	0.01020	0.02569	2.520
	0.01530	0.03776	2.468
	0.02040	0.05066	2.484
$HClO_4$	0.00510	0.01246	2.443
	0.01020	0.02559	2.508
	0.01020	0.02497	2.447
	0.01530	0.03803	2.485
	0.02040	0.05104	2.502

TABLE 2

Electrolyte effect at 0°C. in lithium chloride solutions

HCl	LiCl	k (OBSERVED)	$k/C_{\text{acid}} = k_{H_3O^+}$
moles per liter	*moles per liter*		
0.010096	0.040	0.02620	2.60
0.010096	0.090	0.02819	2.80
0.010096	0.140	0.02967	2.95
0.010096	0.190	0.03164	3.13
0.010096	0.240	0.03296	3.27
0.010096	0.290	0.03432	3.40
0.010096	0.390	0.03781	3.75
0.010096	0.490	0.04182	4.14
0.010096	0.590	0.04564	4.52
0.010096	0.790	0.05406	5.35
0.005048	0.995	0.03185	6.31
0.005048	1.495	0.04782	9.47
0.005048	1.995	0.07310	14.48
0.003029	2.497	0.06588	21.75
0.002019	2.998	0.06892	34.13

and that equation 1 is only approximately in agreement with experiment even in dilute solution.

The value of B apparently decreases with concentration and becomes fairly constant at the higher concentrations. If the assumption that equation 2 holds is correct, the change in B must be due to the fact that equation 3 does not express the change of the activity coefficient of the ions with increasing electrolyte concentration. The more exact form of equation 3 is

TABLE 3

$k_{H_3O^+}$ at 0°C. for various electrolytes

ELECTROLYTE CONCENTRATION	$NaCl$	KCl	$NaClO_4$	$C_6H_5SO_3Na$	p-$C_6H_4CH_3SO_3Na$	$LiNO_3$	$NaNO_3$	KNO_3
moles per liter								
0.05	2.58		2.61	2.55	2.58			
0.10	2.76	2.79	2.84	2.63	2.68	2.77	2.72	2.74
0.15			3.04	2.73	2.74			
0.20	3.08	3.11	3.21	2.81	2.82	3.05	3.01	2.89
0.30	3.43		3.60	2.89	2.93	3.30	3.19	3.09
0.40	3.73	3.73	4.04	3.06	3.06	3.55	3.50	3.31
0.50	4.08		4.52	3.19	3.23	3.85	3.76	3.51
0.60	4.48	4.37	5.01	3.35	3.40	4.14	3.95	3.73
0.70				3.47	3.49			
0.80	5.27	5.08	5.98	3.65	3.63	4.80	4.43	4.08
0.90				3.75	3.75			4.27
1.00	6.16	5.74	7.08	3.97	3.80	5.51	4.99	4.49
1.10								4.62
1.20								4.88
1.25	7.47			4.45				
1.50	9.09	7.95	10.44	5.04		7.85	6.51	
1.75	10.83		12.43	5.62				
2.00	13.06	10.96	15.15			10.98	8.32	
2.25	15.69		18.49					
2.50	18.90	14.34	22.43			15.06	10.60	
3.00	27.64	19.42	31.50			21.08	12.97	

$$- \log f = \frac{A\sqrt{C}}{1 + \kappa b} + \beta' C \qquad (5)$$

where b is the mean ionic diameter of the given ion and the ions in the solution. Other equations of this type have been used by other investigators (13), but in all cases for this type of reaction the resulting equation for the salt effect has the same form as equation 1.

TABLE 4

$$\frac{\log k_{H_3O^+} - \log k^{\circ}_{H_3O^{\circ}}}{C} = B$$

ELECTROLYTE CONCENTRATION	NaClO$_4$	LiCl	NaCl	KCl		LiNO$_3$	NaNO$_3$	KNO$_3$	p-C$_6$H$_4$(CH$_3$)SO$_3$Na	C$_6$H$_5$SO$_3$Na
moles per liter										
0.05	0.50	0.46	0.40[0.49]					(0 54)	0.40	0.30
0.10	0.61[0.54]	0.55	0.49(0.53)[0.50]	0.49	0.$\overline{\underline{46}}$	0.51	0.43[0.38]	0.46[0.41]	0.36	0.28
0.15	0.60	0.52	(0.53)						0.31	0.29
0.20	0.57[0.52]	0.51	0.49(0.56)[0.45]	0.48	0.$\overline{\underline{46}}$	0.46	0.43[0.35]	0.35(0.46)[0 36]	0.29	0.28
0.25		0.49								
0.30	0.54	0.47	0.48			0.42	0.37	0.33	0.25	0.23
0.40	0.53	0.46	0.45	0.44	0.$\overline{\underline{45}}$	0.39	0.38	0.32	0.24	0.23
0.50	0.53	0.45	0.44			0 39	0.37	0.31	0.23	0.22
0.60	0.51	0.44	0.43	0.41	0.$\overline{\underline{44}}$	0.37	0.34	0.30	0.23	0.22
0.70									0.22	0.21
0.80	0.48	0.42	0.41	0.39		0.36	0.32	0.27	0.21	0.21
0.90								0.26	0.20	0.20
1.00	0.46	0.41	0.40	0.37	0 $\overline{\underline{39}}$	0.35	0.31	0.26	0.19	0.21
1.10								0.25		
1.20								0 25		
1.25			0.38							0.20
1.50	0.42	0.39	0.38	0.34	0.$\overline{\underline{35}}$	0.33	0.28			0.21
1.75	0.40		0.37							0.20
2.00	0.39	0.38	0.36	0.32	0.$\overline{\underline{32}}$	0 32	0.26			
2.25	0.38		0.36							
2.50	0.38	0.38	0.35	0.31	0.$\overline{\underline{31}}$	0.31	0.25			
3.00	0.37	0.38	0.35	0.30	0 $\overline{\underline{31}}$	0.31	0.24			

The values in ( ) are from the data for diethyl acetal given by Brönsted and Wynne-Jones; those in [ ] are for dimethyl acetal from the data of Brönsted and Grove; those in $\overline{\underline{\quad}}$ are from Kilpatrick and Chase for diethyl acetal.

The temperature coefficient

The acetal reaction is so sensitive to hydrogen ion that $k_{H_3O^+}$ cannot be determined accurately by direct measurement above 0°C. The method employed was the two-thermostat method of Rice and Kilpatrick (12). Portions of the same solution were placed in two similar dilatometers in thermostats at 35°C. and 25°C., respectively. The temperature interval was determined by a calibrated resistance thermometer, and the thermostats were controlled to ± 0.005°C. Equivalent portions of acetal were added to each and $k_{obsd.}$ was calculated in the usual manner. The quotient k_{35}/k_{25} yielded the temperature coefficient directly. Table 5 gives the results and the energy of activation calculated from the Arrhenius equation.

TABLE 5

Electrolyte effect on the temperature coefficient

HCl (APPROX.)	SALT	k_{35}/k_{25}	E	DEVIATION FROM 22,323
moles per liter	*moles per liter*		*calories*	*calories*
0.0001	—	3.372	22,199	124
0.0002	—	3.402	22,360	37
		KCl		
0.00015	0.10	3.423	22,474	151
0.000125	0.50	3.420	22,458	138
0.0001	1.00	3.447	22,600	277
0.00004	2.00	3.493	22,843	520
0.00004	2.00	3.550	23,139	816
0.00004	3.00	3.449	22,611	288
0.00004	3.00	3.407	22,388	65
0.00004	3.00	3.275	21,666	657
		NaCl		
0.00007	1.00	3.385	22,270	53
0.00004	2.00	3.516	22,963	640
0.00004	2.00	3.323	21,934	389
0.00004	3.00	3.206	21,277	1,046
		$C_6H_5SO_3Na$		
0.0001	1.00	3.326	21,949	374
		KNO_3		
0.00005	3.00	3.325	21,942	381
Average......................		3.395	22,323	±370

Apparently the value of the energy of activation remains constant in the presence of neutral salts within the experimental error of measurement.

DISCUSSION

As already stated the results cannot be expressed by equation 1. Upon examination the deviations are found to be hyperbolic functions of the concentration. Equations which express the experimental results within 2 per cent are given below.

$NaClO_4$ $\log k = 0.392 + 0.62C - (\sqrt{0.0576 + 0.104C^2} - 0.24)$
$LiCl$ $\log k = 0.392 + 0.58C - (\sqrt{0.00292 + 0.0482C^2} - 0.054)$
$NaCl$ $\log k = 0.392 + 0.55C - (\sqrt{0.010 + 0.0535C^2} - 0.10)$
KCl $\log k = 0.392 + 0.53C - (\sqrt{0.0256 + 0.0787C^2} - 0.16)$
$LiNO_3$ $\log k = 0.392 + 0.50C - (\sqrt{0.0049 + 0.0438C^2} - 0.07)$
$NaNO_3$ $\log k = 0.392 + 0.45C - (\sqrt{0.0225 + 0.0639C^2} - 0.15)$
KNO_3 $\log k = 0.392 + 0.43C - (\sqrt{0.0144 + 0.0697C^2} - 0.12)$
$C_6H_5SO_3Na$ $\log k = 0.392 + 0.40C - (\sqrt{0.000225 + 0.0418C^2} - 0.015)$
or
p-$C_6H_4(CH_3)SO_3Na$

TABLE 6

Correlation between velocity constant and acidity function

KCl IN MOLES PER LITER	$\log k$	H_0	$\log k + H_0$
0.00	0 389	1 05	1.44
1.00	0 759	0.88	1.64
2.00	1 040	0.75	1.79
3.00	1 288	0.60	1 88

Hammett (8, 9) has recently tried to show a relationship between the velocity constant of a reaction and the acidity function. He finds that the rate of the inversion of sucrose, and the rate of the hydrolysis of ethyl acetate and cyanamide in salt solution, can be expressed by the equation:

$$\log k + H_0 = \log k_2$$

where k is the velocity constant of the reaction, H_0, the acidity function, is equal to $-\log a_{H^+} f_B/f_{HB}$, and k_2 is a constant. In order to test the relationship for the acetal reaction, our values of $\log k$ and the corresponding H_0 values for potassium chloride solutions determined by Hammett are given in table 6.

The last column shows that $\log k_2$ is not constant. In the case of the inversion of sucrose by trichloroacetic acid Hammett interprets the lack of constancy as indicating general acid catalysis. In the case of the acetal reaction it might seem that catalysis by acids stronger than H_3O^+ exists.

The order of the effect of the anions is $ClO_4 > Cl > NO_3 > RSO_3$, which might favor this view. However, the fact that changing the concentration of the hydrogen ion does not change the value of $k_{H_3O^+}$ argues against this view. If molecule catalysis were present an increase in the concentration of H_3O^+ should alter the ratio of acid molecule to hydrogen ion and $k_{H_3O^+}$, calculated on the assumption that the hydrogen ion is the sole catalyst, should vary. Further evidence against the view that acids other than H_3O^+ catalyze this reaction will be presented in a later paper.

SUMMARY

1. The primary kinetic salt effect of nine salts has been determined for the hydrolysis of diethyl acetal catalyzed by strong acids in aqueous solution.

2. The temperature coefficient has been determined, and the heat of activation was found to be independent of the electrolyte concentration within the experimental error of measurement.

3. The reaction has been calibrated to determine the hydrogen-ion concentration of buffer solutions.

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NEW BOOKS

Raumchemie der festen Stoffe. By W. Biltz. 24 x 16 cm. x + 338 pp. Leipzic: Leopold Voss, 1934. Price: unbound, 22.5 RM; bound, 24 RM.

The present volume has been produced by Professor Biltz and a number of collaborators, and is a very illuminating account of the information which may be gained from a study of molecular volumes of large numbers of substances. The approach to the subject is perhaps somewhat old-fashioned in the sense that tabular information concerning atomic and ionic radii as determined by crystal analysis has not been given, although references to crystallographic literature are very full and up-to-date.

The first part of the book gives tabular information on molecular volumes and densities of solids corrected back to absolute zero, and the references to original work set out in detail at the end of each table number several hundred. Although the writers in most instances refer to the type of crystal structure of a particular compound and to the determination of its atomic arrangement, this is as far as the author goes in presenting the more modern physical results. The book is of a distinctly different type than Hassel's recent *Krystallchemie* and covers a much greater range of substances in a more general way. The considerations of radius-ratio and the additive laws for atomic volumes and atomic radii do not perhaps receive quite so much attention as some readers may wish.

The book seems to fall between the entirely tabular type and that of a treatise, with the consequence that the lack of a substance index of any kind makes it a little difficult to use as a detailed work of reference. There is no question, however, that it is an extremely valuable compilation, and the excellent diagrams summarize the more important conclusions arrived at. The end-cover contains a detachable sheet of atomic and ionic volumes set out in the form of the periodic table; this should prove very valuable for quick reference.

J. T. Randall.

Thermionic Emission. By A. L. Reimann. 23 x 15 cm.; xi + 324 pp. London: Chapman and Hall, 1934. Price: 21s.

The subject of thermionics is one which has attracted a good deal of interest during the last thirty years, but it is only very recently that a more complete understanding of the mechanism of electron emission by heated bodies has come about. The application of modern quantum statistics to the problems of metallic conduction and the properties of semiconductors has given us a much clearer insight into the fundamentals of thermionic emission by clean metals and oxide cathodes, respectively. Dr. Reimann's book, whilst preserving an admirable balance between theory and experiment, has not neglected to give considerable space to the pioneer work of Richardson, H. A. Wilson, and others, which did so much to set the subject on its feet. The outlook of the book is entirely fundamental and physical, and the author has wisely left accounts of the obvious practical applications of his subject to others. The techniques of preparing the various thermionic emitters for accurate physical measurement are dealt with in a very clear way; to the practising physicist as well as to the theoretician and student the book is certain to be as valuable as it is timely.

The main items of the book deal with electron emission from clean metals, from contaminated metals, and from oxide cathodes; in addition there are chapters on the emission of ions and modern general theory of electron emission. To the reader not so interested in the detailed presentation of the subject there is an introductory general survey of sixty-seven pages, which should be of great value to physical chemists. Perhaps in a later edition Dr. Reimann might even extend and simplify this chapter a little, as many of the conceptions and arguments may be a little difficult for the non-specialist to grasp on a first reading. A section of the work which may be of more special interest to readers of this journal is concerned with the electron emission from contaminated metals such as cesium on tungsten (W–Th), barium on oxygenated tungsten (W–O–Ba) etc. The book contains considerable information not available elsewhere on this aspect of thermionics; it is well produced and printed, and it possesses the rare virtues of being well-written and indexed.

J. T. Randall.

Strahlentherapie in kolloidchemischer Betrachung. By R. E. Liesegang. 25.5 x 18.5 cm. 46 pp., being pp. 871 to 914 of the Textbook of Medical Colloid Therapy, by Drs. L. Lichtwitz and R. E. Liesegang and Prof. Dr. Karl Spiro. Dresden: Verlagsbuchhandlung Theodor Steinkopff, 1934. Price: 3.00 RM.

This small monograph consists largely of tabulated results of various related publications, dealing with the effects of radiation (light, ultra-violet, x-rays and gamma rays) upon living tissue, considered from the aspect of colloid chemistry. In a short preliminary note the view is advanced that the evolution of species and the non-survival of prehistoric species may be due to the change of type of the radiation incident on the surface of the earth. The action of radiation of different wavelengths upon purely inorganic colloids is first considered on the basis of tabulated findings of various investigators, and the results are briefly discussed from the aspect of molecular charge and photochemical action. Further tabular data are given in respect to the action of radiation on various proteins, which come into question in physiological processes, the "heat point" theory of Dessauer being introduced. Similarly the effects of radiation upon ferments and their action is discussed, followed by a section on the action upon bacterial cultures. This leads to sections of more direct interest to the practical medical radiologist as to the effects of radiation upon the blood, protozoa, egg and ovarian tissues, and isolated organs. Finally the effects upon living skin and carcinomatous tissues are tabulated and briefly discussed.

The monograph, being largely in tabular form, will be of assistance even to those not reading German, but the subject matter is of limited interest, being practically addressed to the few medical radiologists carrying on intense radiation treatment of cancer and other diseases, rather than to those interested in the underlying biochemical phenomena.

B. J. Leggett.

Das Wasserstoffisotop. By R. Frerichs. Ergebnisse der exakten Naturwissenschaften, Sonderabdruck aus Band XIII (not sold separately). 23 x 15.5 cm.; pp. 258–309. Berlin: Julius Springer, 1934. Price: unbound, 28 RM; bound, 29.40 RM.

This small monograph gives a good account of the investigations on heavy hydrogen which had been carried out to the first part of 1934. Considerable attention is devoted to the method of separation. The physical properties are next considered, including nuclear properties and disintegration by the D-nucleus. Something is said of the isotope H^3. The molecules HD and D_2 and the equilibrium between them are dealt with. The rest of the material is mainly concerned with the physical and chemical properties of heavy water. The article is illustrated and provided with a bibliography of 186 items, which may perhaps illustrate the active interest in the new isotope shown in such a short period of time.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 2. 26 x 18 cm.; vi + 285–450 pp. Berlin: Verlag Chemie, 1934. Price: 34 RM. Subscription price: 22.50 R.M.

The volume deals with the electrochemical properties of aluminum, with its reactions with non-metals, metals, compounds of non-metals (including corrosion) and metals, solutions, and organic compounds; with the hydrolysis of aluminum salts; and with the qualitative and quantitative analysis of aluminum, and the methods of testing the corrodibility of the metal. The subjects are treated very thoroughly and with references to the literature. The volume maintains the high standard of the work in general and includes a good deal of information of physicochemical interest.

J. R. PARTINGTON.

Einführung in die Lehre von den Kolloiden. By H. BECHHOLD. 23.5 x 16 cm.; 160 pp. Leipzig: Steinkopff, 1934. Price: 10 RM.

This small volume contains a series of chapters dealing with various properties of colloid systems and written by different authors; the introductory chapter was written by Dr. Bechhold. Dr. Hock deals with the methods by which colloid particles can be identified in properties with macro-molecules as well as their assemblage in sols and gels. Two chapters were contributed by Dr. Heymann on interfaces and the electrical properties of colloid systems. The preparation and purification of colloids are discussed by Drs. Schwarz and Erbe, whilst two chapters on the optical properties and x-ray examination of colloid systems were written by Drs. Hauser and Brill.

Whilst the book scarcely attains the ideal aimed at by the editor, viz., a complete survey of the present position of colloid chemistry and physics, it is nevertheless very readable and would serve as a general introduction to those who wish to take up the subject. The chapters on the optical properties and x-ray examination are especially to be commended.

E. K. RIDEAL.

The Atom. By J. TUTIN. 14 x 22 cm.; 103 pp. London: Longmans, Green and Co., 1934. Price: 6s.

The conception of the Rutherford-Bohr atom has paved the way for advances in many branches of science; it has also satisfied one of the tests of a useful theory in its ability to predict new facts. Therefore some surprise is occasioned when the claim is made that an "inverted" atom, with the electrons in the nucleus and the massive particles circulating in orbits outside, would serve equally well to explain the facts.

Dr. Tutin makes such a claim in his book, and goes further in stating that his "alternative" atom explains in a simple way many important phenomena of physics and chemistry which are so familiar that they are accepted as though no explanation were necessary. Prominent among these explanations is the distinction between metal and non-metal, a distinction which, though forming the basis of the study of chemistry, finds no expression in the orthodox picture of the atom. In Dr. Tutin's theory, however, atoms of metals are provided with free electrons external to the nucleus.

The most radical change which the new theory suggests is in the mechanism of valency. This, in the orthodox view, is a concern of electrons, and therefore should be able to be correlated with spectral emission. To provide a similar mechanism for both valency and spectral emission implies that those atoms which are chemically most active should be most easily excited optically. That this is not true is well-known. Oxygen, one of the most active chemically, yields a spectrum only with difficulty; the inert gases are notably easy to excite spectrally and yet are assumed, because of their chemical inertness, to have their electrons in very rigid configurations.

It appears to the reviewer that on these grounds any alternative atom merits close examination.

Let us see how Dr. Tutin finds an alternative. He notes that it is unsatisfactory to have (1) an electronic mechanism for both valency and spectral emission, (2) no distinction between metal and non-metal. He overcomes the latter by allotting free electrons to metals, i.e., by furnishing a mechanism associated with ease of spectral emission. But do the properties of elements warrant a close parallelism between ease of spectral emission and metallic nature? Dr. Tutin's argument seems to suggest so, and yet his scheme does not show it (radon with twenty-two free electrons should surely be a metal). Has he not removed one difficulty only to raise another?

The "inverted" atom of Dr. Tutin is not so simple to grasp as the name suggests. It is not merely a "mirror image" of the Rutherford-Bohr one. The nucleus consists of electrons only, and their number is given by the atomic number of the element; but around the nucleus we may have isolated protons or electrons, or combinations of these in one or more of six possible groupings. (The stability of the nucleus is not discussed, but "since extranuclear electrons are repelled by the nucleus, they can only be tied to the atom by attaching themselves to groups of protons.") At the outset, therefore, the author has made *ad hoc* assumptions flexible enough one would imagine to allow him to "explain" anything. It could be justified only if it gave a neat and consistent picture of the elements of the Periodic Table. But a glance at the structures suggested reveals no such consistency. There is little resemblance between the structures of related elements, e.g., the halogens, nor even between the structures of the inert gases.

The weakest point in Dr. Tutin's essay is in his treatment of isotopes. This is all but shelved by his assumption that single protons may be used as constructional units and placed near the nucleus where they play no part in atomic union. The difference between an atom and its isotope, however, does not concern protons only, but an equivalent number of electrons. What happens to these? Dr. Tutin does not say, but in the solitary example discussed by Li^6 and Li^7, it appears that Li^7 has a free electron whilst Li^6 has not. According to his theory the former should conduct electricity, whereas the latter should not. Dr. Tutin does not make the prediction, although there are grounds for believing that it may soon be possible to test it experimentally.

The impression given by the book is that it is immature in that it deals superficially with a vast number of properties without adequate discussion of any one of them; and that the space devoted to justifying the Law of Causation would have been better used to meet the objections likely to be raised by the champions of the Rutherford-Bohr atom. It is difficult to say for whom the book was written. The general student is not competent to weigh the evidence produced; the specialist would not be satisfied with vague claims of what the theory involves, but would need a much more detailed discussion of each point raised.

JOHN A. CRANSTON.

Journal of the Institute of Metals. Volume LV (Proceedings). 304 pp. 17 plates. Edited by G. Shaw Scott, M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Price: £1.11s.6d. plus 6d. postage inland, 9d. postage overseas.

The latest volume issued by the Institute of Metals is essentially a record of the papers presented at the Manchester Autumn Meeting and of the discussions on these papers. A special contribution is the Autumn Lecture, which deals with the work of Walter Rosenhain, a distinguished past president of the Institute, who died in 1934. A complete record of his published work forms a valuable appendix to the lecture; the list covers five closely printed pages. A great part of the present volume consists of a very practical series of communications, together with a general discussion, on the improvement of white bearing metals—a subject of much interest to engineers at the present time.

Resonance Radiation and Excited Atoms. By A. C. G. MITCHELL and M. W. ZEMANSKY. 338 pp., 84 figures, and 56 tables. New York: The Macmillan Co., 1934.

The book is an exhaustive treatise on this special topic in molecular physics. In Chapter I such parts of modern spectroscopy are introduced as are needed in the further development of the subject. The sources of resonance radiation, the resonance lamps, are described and hyperfine structure of line spectra and resonance radiation are covered. Physical and chemical effects connected with resonance radiation are dealt with in Chapter II. Some of the topics included are: stepwise radiations, sensitized fluorescence, interaction of excited atoms with molecules and attendant chemical effects. The principle of microscopic reversibility or of detailed balancing or complete equilibrium is fully discussed in a most satisfactory manner. In Chapter III the authors cover the topic of absorption of light and the determination of the life time of the resonance state. Some of the sections are: the absorption coefficient of a gas, the emission and diffusion of resonance radiation, absorption within a resonance line as compared with the absorption of its edges, the magneto rotation and dispersion of the edges. Chapter IV contains an account of the collision processes involving excited atoms, the broadening of spectral lines, and the quenching of resonance radiation, while Chapter V concerns the phenomenon of polarization of this type of radiation. An appendix contains several pertinent derivations of formulas and tables of functions. Each chapter ends with a complete bibliography of the subject matter dealt with, giving in alphabetical order references to the original literature. The style is simple and the story is unfolded in a direct and forceful manner. All students of modern atomic, molecular, and chemical physics will welcome this volume, as it brings together the complete literature of an interesting and important development of modern spectroscopy.

GEORGE GLOCKLER.

The Sub-Atom. By WILLIAM M. VENABLE. 148 pp.; 11 figures. Baltimore: The Williams and Wilkins Co., 1933.

The author tries to establish a different theory of matter than is held by modern chemists and physicists. He does not like the Bohr–Rutherford model of the atom with its positive massive center and its planetary electrons. He says: "Atoms are revealed as composite bodies made up of aggregations of ions each with a positive charge $+e$, accompanied with its negative charge $-e$. These smaller ions each with its electron are designated sub-atoms." The book is the product of an active mind trying to change every concept with which it comes in contact. The alpha particle has mass 2 and not 4 and a charge $+e$ and not $2e$. The modern concept of light emission and absorption by atoms is no good. Hydrogen spectra found as impurity in spectroscopic investigation are not due to such impurity at all, but arise from the fact that hydrogen is contained in all other heavier elements as a sub-element. One wonders why the author condescends to use any current concept at all. He probably could not think of replacements or he would have done so. To anyone even only superficially acquainted with modern chemical physics, the book is very annoying. However, from another point of view, it is interesting reading. It stimulates one's interest in reviewing the arguments which have led to our modern concepts of atomic and molecular structure.

GEORGE GLOCKLER.

Theoretical Physics. Vol. II. Electromagnetism and Optics. (Maxwell-Lorentz). By W. WILSON. 315 pp.; 78 diagrams. New York: E. P. Dutton and Co., 1933.

In this second volume the author continues his treatment of theoretical physics based on notes from lectures to university students. He covers electrostatics (Chapter I), polarization in dielectric media (Chapters II and III), magnetostatics (IV), electromagnetism (V and VI), thermoelectric currents (VII), Maxwell theory (VIII), and electron theory (IX and X). The very nature of the subject demands the mathematical treatment the author accords it. In his preface he points out the special form of the electromagnetic field equations in which an unusual notation brings out a four-dimensional appearance suggestive of relativity theory. This material covers 234 pages, leaving only about 80 pages for five chapters on optics. These cover geometric optics (XI), physical optics, interference and diffraction (XII), Huygens' principle (XIII), propagation of light in crystalline media, polarized light (XIV), and general questions concerning the propagation of light (XV). Some of the chapters have a bibliography appended, where the interested reader can find the best known references concerning the material discussed. This seems particularly fortunate in the latter chapters, for the treatment there is certainly concise and not one word is wasted. This treatise on theoretical physics should appeal particularly to chemists as a reference-set where they can expect to find precise statements concerning the various topics discussed.

GEORGE GLOCKLER.

ELECTROKINETICS. XIV

A Critical Comparison of Electrophoresis, Streaming Potential, and Electrosmosis[1]

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There have been various attempts to check the different methods of measuring electrokinetic potentials against one another. Thus Saxén (18) working with clay plates found good agreement between streaming potential and electrosmosis. Kanamaru (16), on the other hand, was unable to find agreement between electrosmosis and streaming potential for diaphragms made of cellulose. Briggs (5) attempted to check with streaming potential technique the values obtained by Abramson (1), using quartz particles coated with egg albumin. Excellent agreement was found. Since, however, both of these workers used relatively impure samples of egg albumin from completely different sources and also different buffer systems, the agreement appears to be fortuitous. This conclusion is borne out by subsequent observations by Abramson and Grossman (3). Abramson (2) has found good correspondence between electrosmosis and electrophoresis, using protein-covered surfaces.

It appeared worth while to the author to reëxamine the whole question and compare systems as nearly alike and under as similar conditions as possible.

EXPERIMENTAL

The streaming potential apparatus used was the same as that reported in a previous communication by the author (7) and was arranged in the same fashion, except that two capillaries were used in series in order to increase the streaming potential.

The electrophoretic cell was a radical modification of the one reported by Buzágh (12), and a further modification of the one used by Bull and Söllner (11) and also by Bull, Ellefson, and Taylor (8). No complete description of this apparatus has been published. It therefore seems worth while to describe the cell, since it combines the virtues of being inexpensive, simple in operation and construction, and easily cleaned. It consisted simply of a strip of plate glass into which a groove 1 mm. deep and 1.5 cm. wide had been cut, ground and polished lengthwise on its face. Small holes were ground through the strip of glass about 2 cm. from each end. These holes had glass tubes sealed into them and served as inlet and outlet for the cell. The electrodes consisted of copper wire imbedded in plaster of Paris made with half-saturated potassium chloride and inserted in the ends of the groove. The plaster was smoothed off, a thin cover glass obtained from an old photographic plate was laid over the groove, and the joint between the cover glass and the plate glass was sealed with melted paraffin wax. Melted wax was also poured behind the electrodes. The wax was allowed to solidify and the cell was ready for calibration. (The complete cell is shown in figure 1.) The fitting together of the cell requires only a few minutes so that the cell may be taken apart, cleaned, and put together again with no great trouble. The cell was placed upon the stage of a microscope equipped with a 12.5 × ocular and an 8 mm. objective which combined working distance with sufficient magnification. The thickness of the chamber when filled with water was measured by means of the screw micrometer of the microscope. The copper electrodes were connected to the D.C. source of current. The potential gradient was obtained by measuring the distance between the electrodes, and dividing this into the total potential drop as determined by an accurately calibrated voltmeter. The potential across the cell was usually around 200 volts.

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[1] Paper No. 1280, Journal Series, Minnesota Agricultural Experiment Station. Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

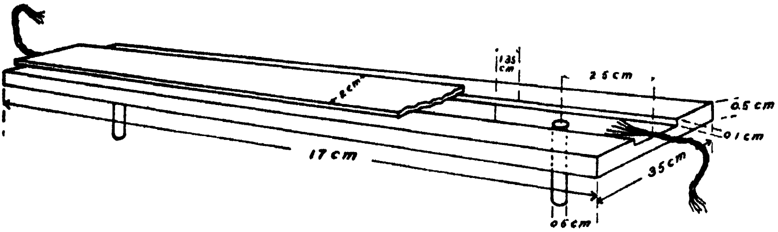

FIG. 1. THE MODIFIED BUZÁGH ELECTROPHORESIS APPARATUS

In accordance with the formulation by Smoluchowski (21), measurements were made at the stationary levels. These stationary levels lie at 0.21 and 0.79 of the total depth of the cell. A series of four readings was made in one direction and a like number in the opposite, until at least sixteen measurements had been obtained at each level. Velocity was measured with a stop watch by determining the time required for a particle in sharp focus to travel between two lines of the ocular micrometer. The electrosmotic velocity was determined by making use of the technique employed by Abramson (2). Sixteen determinations of mobility were made at the half depth of the cell. The electrophoretic mobility was subtracted from these and multiplied by 2. The result is the electrosmotic velocity of the solution. Both the electrophoretic and electrosmotic mobilities are expressed in μ per second per volt per centimeter.

Conductivity was determined with an A.C. galvanometer. This instrument had been previously checked against a 1000-cycle vibrator and earphones. The usual bridge arrangement was used. The 1000-cycle frequency was used to determine the cell constant. The method and values of Parker and Parker (17) were used for the calibration with $N/10$ potassium chloride.

The particles used in the electrophoretic measurements were Pyrex glass particles of about 1 μ in diameter. Pyrex glass was selected instead of quartz to insure the same surface as that of the capillaries which were used in the streaming potential measurements.

Two proteins were used to coat the particles and capillary walls. They were electrodialyzed Bacto gelatin prepared by Sinclair and Gortner with an ash content of 0.05 per cent, and egg albumin made from fresh eggs and crystallized three times from ammonium sulfate, according to Sörensen (19). The egg albumin was subsequently electrodialyzed.

The protein solutions were made up the day before the experiment was to be conducted. This was to allow the solution to come completely to equilibrium. The electrophoretic and streaming potential measurements were always made on the same day and usually within two hours of each other. The temperature was 25° ± 1°C.

Hydrochloric acid was used to bring the protein solutions to the desired hydrogen-ion concentration. The use of the ordinary buffer systems was avoided, owing to the desire to keep the conductivity as low as possible and thus obtain a higher streaming potential. The hydrogen-ion concentrations were determined with a quinhydrone–platinum electrode, using Clark's values for the electrodes.

The streaming potential measurements were conducted first. The entire protein solutions were streamed through the capillaries several times before readings were taken. In all cases at least twenty-one readings were made at different pressures and in reverse directions. Upon the completion of the streaming potential measurements the protein solution was removed to a flask, a portion poured out, and powdered Pyrex glass added. This was allowed to stand fifteen minutes, and the electrophoretic velocities determined.

The ratio between the zeta potential as determined by streaming potential and electrophoresis was obtained by use of the following formulas:

$$\zeta_s = \frac{4\pi\kappa H\eta}{DP} \text{ (streaming potential)} \qquad (1)$$

TABLE 1

EXPT. NO.	SYSTEM	pH	$\kappa \times 10^6$	H/P	$\kappa H/P \times 10^5$	V_e*	V_e†	$\frac{\zeta_s}{\zeta_c}$‡§	$\frac{\zeta_e}{\zeta_c}$¶	$\frac{\zeta_s}{\zeta_e}$
			ohms^{-1}	*mv. per cm. of* Hg		*μ/sec./volt/cm.*	*μ/sec./volt/cm.*			
1	0.0672 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.00	6.87	4.33	29.70	2.06		1.09		
2	0.0672 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.03	6.65	4.095	27.20	2.348		0.88		
3	0.134 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.49	5.35	4.353	23.30	2.087		0.85		
4	0.168 per cent egg albumin in 4 × 10^{-4} *N* HCl	4.40	6.58	3.882	25.60	2.123		0.91		
5	0.168 per cent egg albumin in 5 × 10^{-4} *N* HCl	4.26	8.35	3.25	27.20	2.596		0.79		
6	0.202 per cent egg albumin in 3.5 × 10^{-4} *N* HCl	4.17	10.85	2.38	25.80	2.000	1.882	0.98	0.94	1.04
7	0.158 per cent gelatin in 4 × 10^{-4} *N* HCl	4.24				1.553	1.72		1.11	
8	0.174 per cent gelatin in 5 × 10^{-4} *N* HCl	4.12	12.85	1.82	23.40	1.632	1.682	1.08	1.03	1.05
9	0.166 per cent gelatin in 6.3 × 10^{-4} *N* HCl	4.01	15.22	1.779	27.10	1.852	1.624	1.11	0.88	1.26
10	0.166 per cent gelatin in 7.0 × 10^{-4} *N* HCl	3.77	16.30	1.238	20.20	1.876	1.794	0.81	0.96	0.84
11	0.180 per cent gelatin in 7.5 × 10^{-4} *N* HCl	3.68	17.70	1.031	18.25	2.03	2.00	0.68	0.99	0.69
12	0.175 per cent gelatin in 7.5 × 10^{-4} *N* HCl	3.62	18.50	1.965	36.40	2.06	2.26	1.34	1.10	1.22
13	0.226 per cent gelatin in 8.0 × 10^{-4} *N* HCl	3.72	18.00	1.339	24.10	1.87	1.98	0.98	1.06	0.93
14	0.207 per cent gelatin in 6.5 × 10^{-4} *N* HCl	3.82	14.48	1.547	22.40	1.86	1.92	0.91	1.03	0.88
15	0.219 per cent gelatin in 5.0 × 10^{-4} *N* HCl	4.01	12.30	1.784	22.0	1.72	1.72	0.97	1.00	0.97
Average for protein-covered surfaces								0.97	1.01	0.99
Quartz in 2 × 10^{-4} *N* NaCl					84.97	4.317		1.48		
Quartz in 2 × 10^{-4} *N* NaCl					84.97	4.40		1.47		
Cellulose in 2 × 10^{-4} *N* NaCl					13.75	3.71		0.28		

* V_e = electrophoretic mobility. † V_e = electrosmotic mobility. ‡ ζ_s = potential from stream potential. § ζ_c = potential from electrophoresis. ¶ ζ_e = potential from electrosmosis.

$$\zeta_e = \frac{4\pi\eta V}{DX} \text{ (electrophoresis)} \tag{2}$$

where κ is the conductivity in reciprocal ohms, H the streaming potential, η the coefficient of viscosity, P the pressure forcing the liquid through the capillaries, X the potential gradient across the electrophoretic cell, D the dielectric constant, and V the velocity of the particle.

Dividing equation 1 by equation 2

$$\frac{\zeta_s}{\zeta_e} = \frac{\kappa H}{P}\frac{X}{V} \tag{3}$$

and introducing the proper constants to convert the ordinary units into electrostatic units we have

$$\frac{\zeta_s}{\zeta_e} = 7.57 \times 10^3 \frac{H\kappa}{P}\frac{X}{V} \tag{4}$$

This equation was used to calculate the values given in table 1.

It was thought that it might also be interesting to compare the two methods using surfaces which were not covered with protein. Accordingly, some of the same quartz used by Bull and Gortner (10) in their study on particle size was suspended in $2 \times 10^{-4}M$ sodium chloride and its electrophoretic velocity determined. The true streaming potential was assumed to be given by the quartz where the potential no longer varied with the particle size, that is, at the largest size of particle. No decided trend in speed was noted between the various particle sizes. The electrophoretic speed of cellulose fibers was also measured. The cellulose was the same as that used by Bull and Gortner (9), and the streaming potential data was taken from their paper.

DISCUSSION

Although there are only fifteen ratios reported for the relation between streaming potential and electrophoresis for protein surfaces, actually these represent a great many measurements. There have been 480 electrophoretic measurements and 294 streaming potential determinations, so the whole takes on the color of a statistical analysis. The ratio comes out to be 0.97, which within experimental error may be considered equal to 1. The ratio of the electrophoretic potential to the electrosmotic potential is very close to 1, which is in good agreement with the results of Abramson (2). There is also satisfactory agreement between the electrophoretic potential and the electrosmotic potential. Thus it is seen that with protein-coated surfaces there is good correspondence between the three methods of determining the electrokinetic potentials. This lends support to the customary theoretical treatment of these phenomena, and would seem to support the factor of 4 in the equation for electrophoresis as derived by von Smoluchowski (20) and Henry (14).[2]

The values for quartz and cellulose are quite disturbing. There is indeed very little resemblance between the electrophoretic values and the streaming potential results. It is not certain that the surface potential on the larger quartz particles is the same as that for the very small ones used in the electrophoretic study, though there was no evidence of any very decided trend in the potential as determined with electrophoresis. The results obtained from these measurements seem to bear out the factor of 6π, instead of 4π as proposed by Debye and Hückel (13, 15). The values obtained for cellulose by the streaming potential method are much too low. If the results of Kanamaru (16) be accepted for the streaming potential on cellulose, the agreement between the streaming potential and electrophoresis becomes much better; however the electrosmotic results then fall out of line. It may be that the small values for the streaming potential with cellulose are due to the diminished pore size in the diaphragm packed tightly with cellulose. This is in keeping with the experimental results of White, Urban, and Van Atta (22) and also of Bull and Gortner (10) and with the theoretical considerations of Bull (6) and also of Bikerman (4). More investigation of surfaces which derive their charge by adsorption rather than by dissociation, as with proteins, is badly needed.

SUMMARY

1. A new electrophoretic cell has been described.
2. The electrophoretic, electrosmotic, and streaming potential methods

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[2] Henry proposes the equation

$$U = \frac{3\mu}{2\mu + \mu'} \frac{\zeta DX}{6\pi\eta}$$

for the electrophoretic mobility, where μ is the specific conductivity of the dispersions medium, μ' is the specific conductivity of the particle, and the other letters have the same significance as previously noted. It can be seen that when dealing with non-conducting particles the factor for the equation becomes 4π. With highly conducting particles the mobility should approach zero. This has not been generally observed. Henry explains this by assuming that the particles become polarized and are in this fashion rendered non-conducting. Bull and Söllner (11) have published mobility data obtained with mercury particles in a mercurous nitrate solution. These particles should be non-polarizable. Substituting approximate values in the Henry equation for the specific conductivities of the mercury and a 0.001 M mercurous chloride solution, we find that the equation becomes approximately

$$U = 50 \times 10^{-6} \frac{\zeta DX}{6\pi\eta}$$

This indicates that the mobility should be in the order of 1/100,000th of that observed. This represents a large discrepancy between the theoretical and experimental results.

of measuring the electrokinetic potentials have been compared, using the same solution and surface.

3. Good agreement was found when dealing with protein-coated surfaces.

4. Poor correspondence was found between electrophoresis and streaming potential for quartz and cellulose surfaces.

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A COMPARISON OF THE ELECTROPHORETIC, ELECTROSMOTIC AND STREAM POTENTIAL ISOELECTRIC POINTS AT GLASS AND GELATIN SURFACES[1]

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According to modern conceptions the ionic double layer responsible for electrokinetic phenomena consists of a sheet of ions containing an excess of either positive or negative charges rigidly attached to the solid wall, and a second layer of ions in the adjacent liquid containing an equal excess of charges of the opposite sign. The wall (inner Helmholtz) layer does not move under the influence either of an applied hydrostatic pressure or of an imposed E.M.F. The outer layer, according to Stern (13), may be further divided into a diffuse (Gouy) component which is moved by an applied hydrostatic pressure, and a second (outer Helmholtz) component immediately adjacent to the wall layer, which cannot be moved by hydrostatic forces. The potential drop across the diffuse, movable component is the electrokinetic or zeta potential.

Urban, White, and Strassner (14) suggest that although the outer Helmholtz layer is not displaced by hydrostatic forces, it may nevertheless move in an electric field. They point out that, on this assumption, only the outermost or diffuse component contributes to stream potential, whereas both the diffuse and the outer Helmholtz layers contribute to electrosmotic velocity. If u_m is the electrosmotic velocity in the center of a capillary, and u_0 and u_h the velocity of the diffuse and Helmholtz layers, respectively, then:—

$$u_m = u_0 + u_h = \frac{ED\zeta}{4\pi\eta} + \frac{ED(\psi - \zeta)}{4\pi\eta} = \frac{ED\psi}{4\pi\eta}$$

where E = applied E.M.F. per unit length of capillary,
D = dielectric constant,
η = viscosity,
ζ = potential drop across the diffuse layer, and
ψ = potential drop across the entire double layer.

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[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

This leads to the conclusion that when ζ (as measured by the stream potential method) becomes zero, electrosmosis may persist, provided that ψ is not also zero. Further, if ζ and ψ are of opposite sign, stream potential may reverse while electrosmosis continues in the original direction. The symbol ψ here designates the potential difference across the entire double layer and does not refer to the potential measured by the glass electrode, the latter apparently depending, within the range of concentrations studied by us, only on the hydrogen-ion concentration.

These deductions may be tested experimentally by determining the direction and velocity of electrosmosis when ζ, as measured by stream potential, is zero. This paper is concerned only with a comparison of isoelectric concentrations for stream potential, electrophoresis and electrosmosis, respectively; a discussion of the absolute magnitude of the electrokinetic potentials at other concentrations will be deferred.

The literature contains only one record of a direct comparison of the stream potential isoelectric point with electrosmotic or electrophoretic isoelectric points on the same material. Abramson and Grossman (3) found that the hydrogen-ion activity required to stop electrosmosis and electrophoresis in an albumin-covered electrophoresis cell with albumin-covered particles was practically the same as that previously found by Briggs (4) to be isoelectric for stream potential through a diaphragm covered with the same protein.

Isolated observations on isoelectric points of surfaces other than protein, however, do not show the same agreement with the two methods. Elissafoff (7) found a concentration of 1.9×10^{-6} *M* thorium nitrate to be isoelectric for electrosmosis in a quartz capillary and about 7×10^{-6} *M* thorium nitrate for a Jena glass capillary; whereas Freundlich and Ettisch (8) and Kruyt and van der Willigen (9) both found that stream potential in a glass capillary was already reversed at concentrations of 3 to 4×10^{-7} *M* thorium nitrate. The possibility remained, of course, that differences in the kind of glass used might have been responsible for this wide discrepancy.

Powis (11) found that a concentration of 3×10^{-5} *M* thorium chloride was required to reverse the electrophoretic movement of droplets of "cylinder oil," while Bull and Gortner (5) report that 1.2×10^{-6} *M* thorium chloride is isoelectric for stream potential on Nujol. Here again, a difference in the kind of oil used might account for the results.

EXPERIMENTAL

In the present paper, stream potential, electrosmotic, and electrophoretic isoelectric concentrations are obtained of (1) hydrogen ion with gelatin, and (2) thorium chloride, ferric chloride, and aluminum chloride with Pyrex glass.

Electrosmotic and electrophoretic isoelectric concentrations were determined by observing the movement of Pyrex glass particles in a closed Pyrex electrophoresis cell of the flat Northrop-Kunitz type. Abramson (1) discusses the use of such cells for electrosmosis and electrophoresis. The observed velocity of the particles at any given depth in the cell is the algebraic sum of the true electrophoretic velocity plus the electrosmotic velocity at that depth. The true electrophoretic velocity, V_p, is the observed velocity of the particles at 0.211 of the distance from the top or bottom of the cell. The true electrosmotic velocity, V_w, may then be obtained either according to the formula $V_w = 2(V_{\frac{1}{2}} - V_p)$, where $V_{\frac{1}{2}}$ is the observed velocity in the middle of the cell, or according to the formula $V_w = V_0 - V_p$, where V_0 is the observed velocity at the wall of the cell. It was found in preliminary experiments that when the particle velocity was plotted against cell depth a symmetrical parabola was obtained; also that values of V_w as calculated from the two formulas given above showed good agreement. In subsequent experiments, therefore, observations were made only at the bottom of the cell and at 0.211 of the distance from the bottom, and the electrosmotic velocity calculated from the second formula.

In the case of thorium chloride with Pyrex, the electrosmotic isoelectric point was also determined directly by applying an E.M.F. across a Pyrex capillary of 600μ diameter containing varying concentrations of thorium chloride and observing the rise or fall of liquid in the recording arm of the apparatus due to electrosmotic transport across the capillary (Quincke (12)). The two methods gave the same results.

Stream potential determinations were carried out on a Pyrex capillary of 300μ diameter by the method described by White, Urban, and Van Atta (15).

For all isoelectric point determinations on gelatin, solutions which were 4×10^{-4} N with respect to potassium chloride plus hydrogen chloride and which contained 0.01 g. gelatin per liter were used. The pH was varied by changing the proportion of hydrogen chloride to potassium chloride. Measurements of pH were performed by the glass electrode method. Both particles and cell were allowed to stand in contact with the gelatin solution for one hour before measurements were begun, in order to allow the glass surfaces to become coated with the protein. It has been shown repeatedly (Abramson (2); Dummett and Bowden (6)) that many substances, including glass, adsorb a complete coating of gelatin from dilute solutions of this protein, and that such protein-covered surfaces no longer behave like glass surfaces, but rather show the properties of the adsorbed protein. That is, by treating the glass surfaces as described they have in effect been converted into gelatin surfaces, so that it is now possible to study the effect of ions (in this case hydrogen ions) on electrokinetic phenomena at a gelatin surface. To obtain reproducible results with such poorly buffered solutions it was found necessary to increase the length of the side arms on the electrophoresis cell to about 20 cm. on each side in order to prevent diffusion of acid from the electrodes into the flat part of the cell during a series of readings.

Stream potential measurements were made on gelatin-coated glass capillaries, using the same solutions that were used for electrosmosis and electrophoresis. In order to secure complete coating of the capillary in a short time, a more concentrated gelatin solution (0.1 g. gelatin per liter) was run through for a few minutes before the determinations began. At hydrogen-ion activities close to the isoelectric point the stream potential generally required several hours to reach a constant value.

The isoelectric point data are summarized in table 1.

A few words concerning the accuracy and reproducibility of these results may be inserted here. It should be pointed out that the figures listed are not the result of isolated observations near the isoelectric point, but are taken from smooth curves representing electrokinetic potential over a wide range of concentrations. A typical set of curves is reproduced in figure 1. The absolute magnitudes of the electrokinetic potentials obtained by the three methods are not of quantitative significance; we were interested here only in the isoelectric points, and conditions essential to a quantitative measurement of electrokinetic potential were not adequately controlled. The isoelectric concentrations are given only to the nearest whole number, since the curves are not reproducible with greater accuracy than this. For example, on six experiments on the electrophoresis cell, the isoelectric concentration varied between 2 and 4 × 10^{-6} *M* thorium chloride. In two experiments with the Quincke set-up the curve crossed the zero potential line between 2.5 and 3 × 10^{-6} *M* thorium chloride. However, experimental variations in the isoelectric point (due probably to slight contamination of the surfaces or to differences in the time allowed for equilibrium, etc.) do not go beyond these limits; at a concentration of 1 × 10^{-6} *M* thorium chloride, electrophoresis and electrosmosis always

TABLE 1

Isoelectric pH for gelatin and isoelectric ion concentrations with Pyrex glass

	ISOELECTRIC pH FOR GELATIN	ISOELECTRIC CONCENTRATIONS OF $THCl_4$ WITH PYREX	ISOELECTRIC CONCENTRATIONS OF $AlCl_3$ WITH PYREX	ISOELECTRIC CONCENTRATIONS OF $FeCl_3$ WITH PYREX
		M	*M*	*M*
Stream potential	4 75	4 × 10^{-7}	1 × 10^{-6}	1 × 10^{-6}
Electrosmosis	4 75	3 × 10^{-6}	3 × 10^{-6}	3 × 10^{-6}
Electrophoresis	4.75	3 × 10^{-6}	3 × 10^{-6}	3 × 10^{-6}

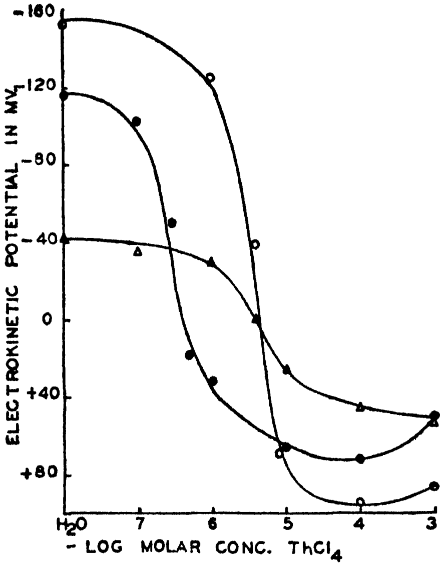

FIG. 1. ELECTROKINETIC POTENTIAL AS A FUNCTION OF $ThCl_4$ CONCENTRATION
○, electrosmosis; ●, stream potential; △, electrophoresis

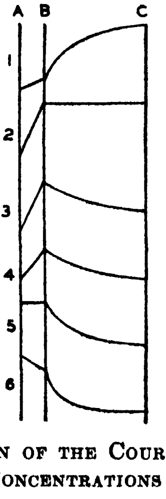

FIG. 2. SCHEMATIC REPRESENTATION OF THE COURSE OF THE POTENTIAL CURVES IN VARYING CONCENTRATIONS OF $ThCl_4$

A represents the solid wall, B the outer Helmholtz layer, C the outer boundary of the diffuse layer. The potential difference between A and C = ψ; that between B and C = ζ. Curve 1 represents the condition in water, where ψ and ζ have the same sign; curve 2, 4×10^{-7} M thorium chloride, stream potential isoelectric; curve 3, 8×10^{-7} M thorium chloride, stream potential reversed; curve 4, 3×10^{-6} M thorium chloride, stream potential reversed, electrosmosis isoelectric; curve 5, 1×10^{-5} M thorium chloride, stream potential and electrosmosis the same, both reversed; curve 6, 1×10^{-4} M thorium chloride, both reversed, electrosmosis greater than stream potential.

have the same sign as in water, while at a concentration of 5×10^{-7} *M* thorium chloride, stream potential is always reversed. With trivalent aluminum and iron the difference in the isoelectric concentrations for stream potential on the one hand and electrophoresis and electrosmosis on the other hand is not so great as with thorium chloride, but no less definite. On the gelatin surfaces all curves crossed the zero potential line at a pH between 4.7 and 4.8.

DISCUSSION

From the experimental data on thorium–glass it is evident that even when the glass surfaces are the same[2] (Pyrex) and the solutions identical, a great difference exists in the isoelectric concentrations of thorium chloride for stream potential on the one hand and for electrosmosis and electrophoresis on the other hand. At concentrations such that stream potential is reversed (between 4×10^{-7} *M* and 3×10^{-6} *M* thorium chloride, electrosmosis and electrophoresis continue in the original direction. This is interpreted to mean that a potential drop may exist across the outer Helmholtz layer when the ζ-potential is zero, and further that the potential of the outer Helmholtz layer may be of opposite sign from that of the diffuse layer. In dilute solutions of thorium chloride, for example, if some of the hydrogen-ions in the outer Helmholtz layer are replaced by tetravalent thorium ions, with their attendant anions in the diffuse layer, then there may actually be an excess of anions in the diffuse component, with a resultant reversal of stream potential. At the same time, if the boundary between mobile and immobile components of the electrical layer, which might here be designated as a triple layer, lies closer to the wall for electrosmosis and electrophoresis than for stream potential, the sign of the former remains unchanged. This sign will be reversed only when the adsorption process has proceeded to the point (with increasing thorium concentration) where the potential at the outer boundary of the diffuse layer is less than that at the wall, which apparently does not take place until the thorium concentration has been increased at least sevenfold above that required for isoelectric stream potential. Figure 2 illustrates schematically this concept of variations in the course of the potential–distance curves as the thorium concentration is increased. Similar considerations hold for the aluminum–glass and iron–glass systems. It is recognized that some colloidal thorium, aluminum, or iron is almost certainly present, but this has no bearing on the reality of a difference in the isoelectric concentration of stream potential on the one hand and of electrosmosis and electrophoresis on the other.

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[2] The surfaces for electrosmosis and stream potential are certainly the same, i.e., fused smooth surfaces. We have also shown (10) that the electrophoretic behavior of broken (particle) and fused (sphere) glass surfaces is the same.

On the other hand, the isoelectric hydrogen-ion concentration for gelatin is the same for electrosmosis, electrophoresis, and stream potential. In this case, when ζ becomes zero, ψ is also zero, and the two are never of opposite sign. Without entering into an adequate discussion of the mechanisms involved in the two cases, it should be pointed out that the layers are probably quite different on the two types of surfaces under consideration. In the case of gelatin the double layer is produced by an ionization process which gives rise only to varying ratios of univalent anions and cations in the solution, the total concentration remaining the same. It is difficult to see how such a process could produce a difference in sign of the outer Helmholtz as compared with the diffuse layer.

SUMMARY

The isoelectric concentration for electrosmosis and electrophoresis on Pyrex glass is found to be for thorium about seven and for aluminum and iron about three times as great as the isoelectric concentration for stream potential on the same kind of glass. The hydrogen-ion isoelectric concentration for gelatin, on the other hand, is the same for electrosmosis, electrophoresis, and stream potential. The results are explained on the assumption that only the diffuse component of the double layer is moved by hydrostatic forces, while both the diffuse and the outer Helmholtz layers move in an electric field.

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IONIC EXCHANGE IN RELATION TO THE STABILITY OF COLLOIDAL SYSTEMS

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INTRODUCTION

Numerous investigators (5, 7) have demonstrated a close relation between the elektrokinetic potential (zeta potential) of colloidal particles and the amount of electrolyte necessary to flocculate the system. A number of years ago Wiegner (10) called attention to the rôle of ionic exchange in modifying the stability of a suspensoid, and it appeared that the significance of the interchange phenomenon had been greatly underestimated by many students of coagulation processes. The present study attempts to clarify the relation among ionic exchange, zeta potential, and flocculation value for colloidal clay systems and to furnish quantitative correlations among these three magnitudes.

EXPERIMENTAL TECHNIQUE

Ionic exchange

The technique of ionic exchange experiments has been fully reported previously (3). In principle, natural Putnam clays were electrodialyzed and the resulting H-clays converted into basic clays (Na-clay, Ca-clay, etc.) by addition of known amounts of hydroxides, except in the case of La- and Th-clays and methylene blue clay, which were obtained by leaching of NH_4-clay with lanthanum nitrate, thorium chloride, and methylene blue chloride. To these basic clays electrolytes were added at various concentrations, and the exchange adsorption determined by analysis of the supernatant liquid. The amount of electrolyte added to the clay sols is expressed in terms of symmetry concentrations, that is, in multiples of the number of milliequivalents of adsorbed ions in the system. In particular, the magnitude of exchange expressed in percentage for the symmetry concentration equal to one ($S = 1$) is called symmetry value. All exchange data used in the present publication are symmetry values and have been reported previously (4).

Zeta potentials

All measurements of migration velocities were made with an ultramicroscope and an open cataphoresis cell as described by Tuorila (8). The cell was improved by introducing removable electrodes to permit thorough cleaning, which reduced the mean error of measurement to 2 per cent. The cell constructed obeyed Smoluchowski's equation strictly. Table 1 contains only a single observed migration velocity for each type of clay, but the average value of the zeta potentials calculated according to the equation

TABLE 1

Data on zeta potentials, adsorption, and flocculation

TYPE OF COLLOIDAL CLAY	MIGRATION VELOCITY* (ALL NEGATIVE)	TEMPERATURE °C.	AVERAGE ZETA POTENTIAL IN MILLIVOLTS (NEGATIVE)	PER CENT RELEASE OF ADSORBED ION (SYMMETRY VALUES)	FLOCCULATION VALUE FOR KCl (IN TERMS OF *S* CONCENTRATIONS)	FLOCCULATION VALUE FOR COMMON CATION AS CHLORIDE (*S*-CONCENTRATION
Li-clay	3.45	30.3	58.8	68.0	21.6	26
Na-clay	3.31	28.9	57.6	66.5	11.2	14.8
K-clay			56.4†	48.7	7.8	7.8
NH_4-clay	3.48	33.2	56.0	50	5.4	4.9
Rb-clay	3.25	30.3	54.9	37.4		
Cs-clay	3.02	30.3	51.2	31.2	5.6	4.2
H-clay	2.84	30.3	48.4	14.5	1.5	0.36
Mg-clay	3.18	30.3	53.9	31.32	2.9	0.69
Ca-clay	3.27	32.8	52.6	28.80	3.0	0.55
Sr-clay	3.06	30.3	51.8	25.76	2.6	
Ba-clay	3.01	30.3	50.8	26.75	2.3	
La-clay	2.74	21.2	45.5	13.96	0.86	
Th-clay	3.11	32.2	50.4 47.1	1.85	0.60	
M.B.-clay	2.57	33.7	40.5		0.0	

* Microns per second per volt per centimeter.

† Interpolated from a corresponding monovalent series (Li, Na, K) of Putnam clay.

$$\zeta = \frac{6\eta\pi\mu}{HD}(300)^2 \tag{1}$$

where ζ = zeta potential,

η = viscosity of the solution (H_2O) in poises,

μ = migration velocity of particle in cm. sec.$^{-1}$, measured at a depth of 0.2113 times the thickness of the cell.

D = dielectric constant (80),
H = potential gradient in volts cm.$^{-1}$, and
300 = ratio of electrostatic unit to practical electromagnetic unit of potential.

Although equation 1 is subject to criticism, we prefer to report the results as zeta potentials rather than migration velocities.

The migration velocity was found to be directly proportional to the potential difference between the electrodes, and appeared to be independent of the size of the particles. As the concentration of the sol increased the velocity decreased, as shown in figure 2. All data reported were measured at a sol concentration of 0.001 per cent on the basis of the weight of H-clay. The sols were kept in stock solutions of 0.5 per cent and 1.0 per cent, and it was observed that after dilution to 0.001 per cent the zeta potentials varied with the age of the diluted sol (figure 1). Final measurements were taken four to six days after dilution. All clays were negative, even the Th- and La-clays, in spite of the fact that addition of thorium chloride or lanthanum nitrate to a K-clay yields positive particles. Evidently during the process of removal of the excess electrolyte by leaching with distilled water the stabilizing chloride ions were replaced by OH^- and HCO_3^- and a negative clay resulted. Somewhat similar observations have been reported by Lottermoser (6). The zeta potential of the Th-clay appears to be too high, as will be demonstrated later.

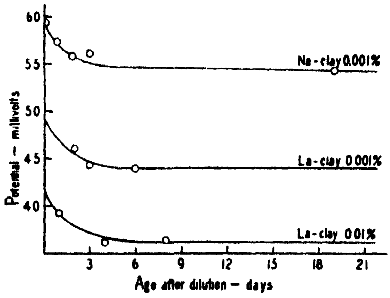

FIG. 1

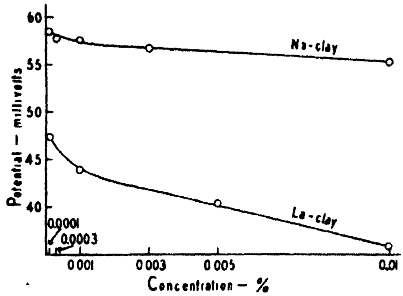

FIG. 2

FIG. 1. EFFECT OF DILUTION AGE ON THE POTENTIAL OF CLAY PARTICLES

FIG. 2. EFFECT OF CLAY CONCENTRATION ON THE ZETA POTENTIAL OF CLAY PARTICLES

Flocculation values

It is difficult to reproduce satisfactorily flocculation values for clay sols because of the great influence of such factors as method of shaking, age of sol, mode of diluting, etc. The following procedure was adhered to rigidly. Into a 75-cc. test tube were placed 5 cc. of 2.66 per cent clay sol (on the basis of H-clay), x cc. of redistilled water, and y cc. of electrolyte solution.

The final volume (5 + x + y) was always 35 cc. For fifteen minutes the tube was gently shaken with a mechanical device and care was taken that no air bubbles formed. Ten cc. of the mixture was then transferred into another 75-cc. tube which contained 25 cc. of water, and both tubes were shaken fifty times. This procedure permitted the determination of flocculation values at two different clay concentrations. In this paper only the values for the second (dilute) system are given. The tubes were put into a thermostat (30°C.), and after six hours the presence or absence of sedimentation was recorded. The flocculation values are expressed in terms of symmetry concentrations, which notation furnishes more instructive figures than does the customary designation as millimoles per liter.

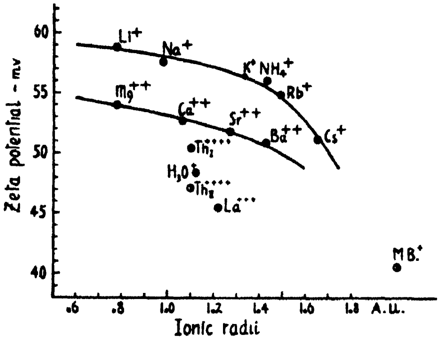

FIG. 3. EFFECT OF CHARGE AND SIZE OF ADSORBED CATIONS UPON THE POTENTIAL OF COLLOIDAL CLAY PARTICLES (Li-CLAY, Ca-CLAY, ETC.)

ZETA POTENTIALS AS INFLUENCED BY CHARGE AND SIZE OF THE ADSORBED CATIONS

In view of the fact that all clays prepared carry the same number of adsorbed cations, namely 60 milliequivalents per 100 g. of clay, the zeta potentials can be directly related to the nature of the ion in the outer swarm of the electric double layer. According to the data in table 1 and the curves in figure 3, certain regular trends are evident, and in particular an ionic charge and size effect come into prominence. *For rare gas type ions of equal size the zeta potentials of the clays tend to be lower as the electric charge of the adsorbed ion is higher.* The restriction of the comparison to ions of equal size is essential because certain mono-clays (e.g., Cs-clay) have lower potentials than some of the di-clays (Mg-clay, etc.). Evidently the statement often found in literature that clays with adsorbed divalent cations have lower potentials than mono-clays is too general, and applies only to ions with equal crystal lattice radii (Goldschmidt's values). The rôle of ionic size can be formulated as follows: *For rare gas type ions of equal valency the zeta potential is the higher the smaller the adsorbed cation.* This observation is in agreement with Wiegner's idea (10), according to which the most hydrated ion (small ions are very strongly hydrated) brings about the highest zeta potential.

On the basis of Helmholtz's classical picture of the electric double layer, the potential is higher as the number of electric charges (e) and the average distance (δ) of the double layer are greater. For ionic crystals such as clay particles, dissociation can be considered as complete (heteropolar linkage) and consequently the magnitude of the zeta potential becomes solely a function of δ. On account of the water shell, the centers of hydrated cations cannot approach the negative wall of the particle as closely as those of the smaller non-hydrated ions. Consequently ions with small crystal lattice radii but great effective sizes (hydrodynamic radii) widen the distance of the double layer and cause high potentials as demonstrated in figure 3.

ZETA POTENTIAL AND IONIC EXCHANGE

The mechanism of ionic exchange can be visualized as follows: Colloidal clay particles are plate-shaped crystals which hold on their surface adsorbed cations. Owing to heat motion and Brownian movement the adsorbed ions are not at rest but oscillate, and at times are at a considerable distance from the wall. If it so happens that on account of Brownian movement a cation of an added electrolyte slips between the negative wall and the positive oscillating ion, the electrolyte cation will become "adsorbed" while the surface ion remains in the solution as an exchanged ion. The more loosely an ion is held the greater is the average distance of oscillation and the greater is the possibility of replacement or, vice versa, the more tenaciously an ion sticks to the surface the less readily it will be released by the cations of an electrolyte added to the colloidal system. The average distance of oscillation corresponds directly to the average thickness of the electric double layer, and on the basis of the picture outlined one would conclude at once *that clays with high zeta potentials contain easily exchangeable ions.*

To test the validity of this conclusion it becomes necessary to learn the ease of replacement of the ions adsorbed on the clays listed in table 1. For this purpose data previously published were used which refer to the very same clay systems used in the present study. The release of the polyvalent cations was accomplished by addition of potassium chloride, while that of the monovalent cations was calculated from the exchange values with NH_4-clay. Since potassium ions and ammonium ions are equally well adsorbed and released, the data permit quantitative comparison.

According to figure 4 it is evident that ions which are easily released are also responsible for high zeta potentials. Lithium and sodium ions are loosely held, and about 70 per cent of them are exchanged by addition of an equal number of ammonium ions (symmetry concentration), while the clays with low potentials (La-clay, Th-clay) have exchange values below 20 per cent. The divalent cations occupy an intermediate position.

Neglecting the wave-like shape of the curves, the general trend of the exchange–zeta potential relation is of parabolic nature as seen in figure 5. The relationship can be satisfactorily described by the equation

$$E = 3.55 \cdot 10^{-10} \zeta^{6.42} \tag{2}$$

where E represents the percentage release of the adsorbed ion at 1 S concentration, and ζ the zeta potential in millivolts. The curve rises in a very pronounced fashion, approximately as the sixth power of the potential.

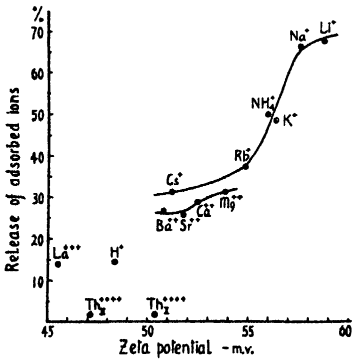

FIG. 4

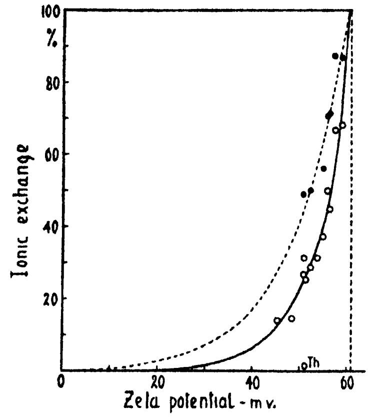

FIG. 5

FIG. 4. RELEASE OF ADSORBED CATIONS IN RELATION TO ZETA POTENTIAL

For example, release of lithium from Li-clay or barium from Ba-clay. Exchange expressed as symmetry values.

FIG. 5. THE INTENSITY OF IONIC EXCHANGE INCREASES APPROXIMATELY AS THE SIXTH POWER OF THE ZETA POTENTIAL

Note the indication of a maximum potential. Black points refer to release by calcium; the white points to exchange with potassium and ammonium.

According to the strong adsorption of thorium the value of the zeta potential of the Th-clay appears to be questionable.

The curves in figure 5 further indicate that the ionic exchange is zero if the zeta potential is zero, in other words, the adsorbed ions are so tightly held that they become an integral part of the particle with a corresponding annihilation of the double layer. Inspection of the upper part of the curve is equally instructive. Since ionic exchange cannot exceed 100 per cent, the trend of the curve strongly suggests that the clay systems investigated possess a definite maximum potential which is slightly above 60 millivolts. These data can be taken as a confirmation of Hevesy's concept (2) and also of Freundlich's statement (1) that the potential of colloidal particles tends to stay below 100 millivolts.

ZETA POTENTIALS IN RELATION TO FLOCCULATION[1] VALUES

The contention of colloid chemists that the zeta potential bears a close relationship to the stability of a colloidal system is well illustrated by figure 6. A series of clays carrying equal amounts but different kinds of cations were flocculated with potassium chloride according to the method mentioned on pages 595–6. It takes much more electrolyte to flocculate a clay with a high potential than one with a low potential. The relation between the flocculation value and the zeta potential also is of parabolic form, showing that the stability increases many-fold with a slight rise in the zeta potential. To flocculate a clay with maximum potential, extrapolation would give a value of about 50 *S*, which corresponds to an electrolyte concentration of 0.0326 *N* potassium chloride for the systems in question.

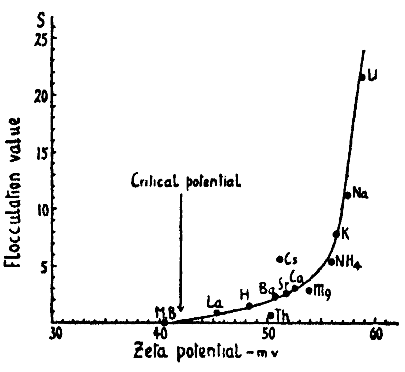

FIG. 6

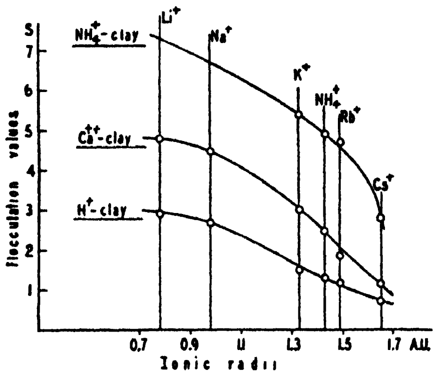

FIG. 7

FIG. 6. FLOCCULATION OF MONO- AND POLY-CLAYS BY POTASSIUM CHLORIDE

The higher the initial potential of the colloidal particle the greater the flocculation value. The critical potential has a value of about 42 millivolts.

FIG. 7. FLOCCULATION VALUES OF VARIOUS CATIONS IN RELATION TO THEIR CRYSTAL LATTICE RADII

The curve in figure 6 tends to cut the X-axis at a potential which is far above zero, and therefore is in accord with the concept of the critical potential, advanced by Powis (7). This value appears to correspond to about 42 millivolts for the type of experimental procedure applied. In confirmation of this magnitude, the methylene blue clay with a potential of 40.5 millivolts sediments completely without the addition of electrolyte.

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[1] "Flocculation" and "coagulation" are used synonymously in this paper.

FLOCCULATION VALUES AS AFFECTED BY CHARGE AND SIZE OF THE FLOCCULATING IONS

Charge of ion

The well-known flocculation rule of Schulze-Hardy, as formulated by Wetham (9), states that the reciprocal flocculation values expressed in moles follow the proportion

$$1_{I} : x_{II} : x^{2}_{III} : x^{3}_{IV} \tag{3}$$

where the Roman subscript denotes the valency of the flocculating ion. This rule is grossly violated in the case of clay systems (table 2). For NH_4-clay and Ca-clay the average flocculation values for the mono- and poly-valent cations yield quotients of the form

$$1_{I} : x_{II} : 2.03x_{III} : 3.21x_{IV} \ (NH_4\text{-clay}) \tag{4}$$

$$1_{I} : x_{II} : 1.76x_{III} : 3.14x_{IV} \ (\text{Ca-clay}) \tag{5}$$

In other words, the polyvalent cations are much less effective coagulators than is indicated by the valency rule. For the two clay systems given, the order of magnitude of effectiveness is much better expressed by a proportion of the type

$$1_{I} : x_{II} : 2x_{III} : 3x_{IV} \tag{6}$$

where the exponents of Wetham's equation have become mere factors.

Size of ion

In figure 7 the flocculation values have been plotted against the crystal lattice radii of the corresponding ions, and it is clearly seen that for a given type of clay the flocculation value is higher as the size of the ion is smaller. The more highly hydrated a cation, the smaller is its efficiency as a coagulator.

FLOCCULATION VALUES AND EXCHANGE ADSORPTION

In the flocculation of ultramicrons, two important cases must be separated. First, the cation of the electrolyte and the colloidal particles possess common ions only (e.g., K-clay + potassium chloride); secondly, the coagulation agent contains only foreign ions with respect to the particle. In the former case flocculation results from repression of the double layer (diminishing of δ). In the second case it constitutes a combination of ionic exchange and the repression phenomenon.

In regard to the common ion effect the data in table 1 vary considerably for different clay systems. Since the osmotic pressures of dilute strong electrolytes of equal normalities vary but little, the great difference in the flocculation values must be attributed to the magnitude of the original zeta potential rather than to the repression efficiency of the various salts. Indeed, the figures for the common ion effect are of the same order of magnitude as the potassium chloride-set values (table 1).

Whenever the flocculating electrolyte contains a foreign cation, exchange adsorption is bound to occur. A comparison between the flocculation values and the ionic exchange data (table 2) points toward an intimate association of the two phenomena. For any specific clay system (NH_4-clay, Ca-clay, etc.) those ions which are poorly adsorbed yield high flocculation values, while cations easily taken in by the colloidal particle coagulate the system at relatively low electrolyte concentrations. The two

TABLE 2

Relation between flocculation values and exchange adsorption

ELECTROLYTE	NH_4-CLAY		Ca-CLAY		H-CLAY	
	Flocculation value (*S*)	Adsorption (*S*)	Flocculation value (*S*)	Adsorption (*S*)	Flocculation value (*S*)	Adsorption (*S*)
LiCl	8.0	32.0	4.8	13.08	2.9	6.6
NaCl	8.0	33.5	4.5	12.74	2.7	6.2
KCl	5.4	51.33	3.0	28.80	1.5	14.5
NH_4Cl	4.9	50	2.5	29.35	1.3	
RbCl	4.7	62.56	1.87	43.85	1.17	28.20
CsCl	2.8	68.78	1.17	50.83	0.73	39.73
HCl	0.98	84.89	0.55	77.80	0.36	50
$MgCl_2$	1.22	65.44	0.59	47.53	0.47	15.78
$CaCl_2$	1.27	63.56	0.55	50	0.47	26.89
$BaCl_2$	1.16	71.67	0.55	52.96	0.35	23.78
$La(NO_3)_3$	0.90		0.47		0.18	
$ThCl_4$	0.75	80.89	0.36	80.24	0.16	

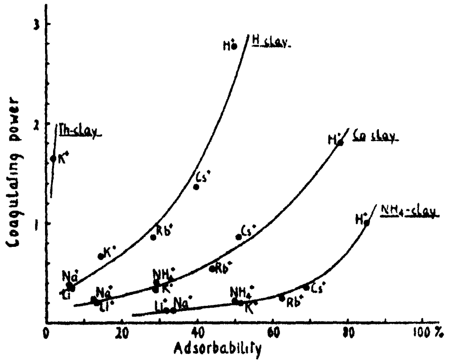

FIG. 8. RELATION BETWEEN ADSORBABILITY OF A MONOVALENT ION AND ITS COAGULATING POWER

sets of values suggest a direct correlation which is of negative exponential type, and the experimental points satisfy the empirical equations

$$F_v = 7.16e^{-0.0332\,E} \text{ (for Ca-clay)} \tag{7}$$

$$F_v = 3.52e^{-0.0431\,E} \text{ (for H-clay)} \tag{8}$$

where F_v represents flocculation value and E the intensity of electrolyte adsorption expressed in terms of symmetry values. The reciprocal of the flocculation value can be taken as an index of the flocculation power of a cation, and the relation of the latter to the adsorbability of the ion is graphically represented in figure 8. The functions are of the form

$$F_p = 0.140e^{0.0332\,E} \text{ (for Ca-clay)} \tag{9}$$

$$F_p = 0.284e^{0.0431\,E} \text{ (for H-clay)} \tag{10}$$

where F_p represents the flocculating power and E the adsorbability (exchange). For the sols tested, the coagulating effect of an ion increases exponentially with its adsorbability. The position of the various curves stresses the fact that for a specific ion its flocculative effect depends largely on the nature of the ion initially adsorbed.

FLOCCULATION BY X-RAYS

The sols listed in table 1 were subjected to x-ray treatment. Th-, La-, and H-clay flocculated after a dosage of 10,503 *r* units, while the di-clays required about double the amount. None of the mono-clays (except H-clay) showed any signs of sedimentation, even after a dosage of 20,503 *r* units. Zeta potentials of treated and untreated samples of Th-, Mg-, H-, and K-clays were measured, and it was observed that in every case the zeta potential was reduced in magnitudes varying from 3.2 to 7.8 per cent. Conductivity measurements failed to reveal the presence of significant amounts of coagulating electrolytes. It must be concluded that the efficiency of x-rays in destroying the stability of the clay systems depends—among other things—on the nature of the adsorbed cation. It appears that the x-rays directly modify the composition of the electric double layer.

MECHANISM OF FLOCCULATION WITH SPECIAL REFERENCE TO THE RÔLE PLAYED BY IONIC EXCHANGE

The data secured in this investigation enables one to draw a rather detailed picture of the significance of ionic exchange in the problem of colloid stability. Hitherto, too much emphasis has been attributed to the behavior of the flocculating electrolyte alone, while the results reported in this paper indicate that the nature of the cations initially adsorbed on the colloid is equally important.

Every electrolyte coagulation is associated with an ionic exchange reaction. Two specific cases of flocculation will be discussed. First, that of a clay system which contains adsorbed monovalent cations of a highly hydrated nature, and secondly, the behavior of particles carrying either non-hydrated monovalent cations or polyvalent ions.

In the first case, which deals with clays containing highly hydrated monovalent ions (e.g., Na-clay), the zeta potential is high because the ions are but loosely held and oscillate over considerable distances. The effective width of the double layer is great (or, the degree of dissociation is high). Although the addition of sufficient amounts of any electrolyte will cause the system to settle out, the magnitude of the flocculation value is a function of the properties of the coagulating cation. If it is also monovalent and strongly hydrated (e.g., Li^+) the extent of ionic exchange will be moderate, in the neighborhood of 50 per cent. The zeta potential becomes but little altered and flocculation has to be brought about by the repression of the double layer (or, decrease in dissociation), which requires large amounts of electrolytes of the order of 15 to 20 *S*.

An entirely different mechanism prevails if the cation of the added electrolyte is monovalent but not hydrated, as Cs^+, or polyvalent as La^{+++}. Under such conditions, ionic exchange assumes a dominating influence. At symmetry concentration, from 75 to 95 per cent of the cations change places. The colloidal particle acquires an entirely new coat consisting of ions which are strongly attracted by the inner layer, and as a result, the zeta potential drops sharply. Very little electrolyte is necessary to repress the new outer swarm of ions to the critical distance which is characteristic of the critical potential. The flocculation values are small, and of the order of 1 *S*.

In regard to the second case, which embraces clays carrying non-hydrated monovalent ions (Cs^+-clay) or polyvalent cations (La^{+++}-clay), the zeta potentials are low to begin with, because the oxygen and hydroxyl ions of the crystal lattice act as powerful adsorbents, and the average oscillation distance of the adsorbed ion is relatively small. Addition of electrolytes possessing hydrated monovalent cations (lithium chloride) will produce a modest exchange only (less than 25 per cent) which, nevertheless, tends to raise the average distance of the double layer and consequently the zeta potential. The stability of the system is definitely augmented, but the repression effect of the electrolyte finally counterbalances the peptization due to ionic exchange and precipitation takes place. The flocculation values are of medium magnitude (2 to 10 *S*), but higher than the common ion values.

If the coagulating cation is of similar nature to the one initially adsorbed (non-hydrated, or polyvalent), ionic exchange assumes again greater dimensions (about 50 per cent) without, however, greatly modifying the zeta potential. Flocculation is accomplished mainly through repression (or decrease of ionization), which is effective at very low electrolyte concentration, often less than 1 *S*.

SUMMARY

1. Zeta potentials of Putnam clay particles depend on the charge and size of the adsorbed ion. For rare gas type ions of equal size, the potential tends to be lower as the valency of the ion is higher. If the charge of the ion is kept constant, the potential is higher as the adsorbed cation (crystal lattice radii) is smaller.

2. Colloidal particles with high potentials carry adsorbed ions which are easily exchangeable. The ease of replacement increases as the sixth power of the zeta potential. Data indicate the existence of a maximum potential which amounts to about 62 millivolts.

3. The flocculation value of a given electrolyte increases potentially with the zeta potential. The critical potential was found to be 42 millivolts.

4. The valency rule of Schulze-Hardy is grossly violated in the case of clay systems. For monovalent cations the flocculation value is the higher the smaller the size of the ion.

5. The flocculating power of a cation is a positive exponential function of its ionic exchange ability.

6. A detailed picture of the mechanism of flocculation in relation to ionic exchange is presented.

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A.C. AND D.C. SURFACE CONDUCTIVITY MEASUREMENTS IN PYREX SLITS[1]

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In a previous communication (5), White, Urban, and Van Atta reported a value of 2.24×10^{-9} mhos for the specific surface conductivity of fused Pyrex glass, in a 5×10^{-4} *M* potassium chloride solution. This value represented an average obtained from D.C. resistance measurements in a number of capillaries of known dimensions. Since the resistances of these capillaries were quite high, i.e., between 10^{10} and 10^{11} ohms, determination of the resistance by means of A.C. was not considered feasible.

In the present paper, surface conductivity measurements in Pyrex slits, carried out both with D.C. and A.C., are described. The slits were obtained by the simple expedient of cracking Pyrex flasks; the width of these slits varied between 0.6 and 16 μ, in different flasks.

DETERMINATION OF LENGTH AND THICKNESS OF THE SLITS

The slit length was determined by means of a pantograph, the magnification being between 8 and 10. The thickness of the glass was measured with micrometer calipers, along the entire length of the slit. An average of these measurements was used for the thickness of the slit.

After the resistance measurements had been completed, potassium ferrocyanide solution was sucked into the slit, which was then immersed in ferric chloride solution. Two parallel blue lines are seen where the slit is open; these indicate the top and bottom of the slit. In the very narrow slits, this method did not give satisfactory results, and the deposit of Prussian blue had to be formed by electrolysis.

APPARATUS

The resistance measurements were carried out in a water bath at 25.00 ±0.01°C. The Wheatstone bridge was a 5-dial Gray instrument, with coils accurate to 0.025 per cent. The A.C. current was supplied by a 1000-cycle motor generator. The d'Arsonval galvanometer (D.C. measurements) had a sensitivity of 10^{-10} ampere.

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A.C. MEASUREMENTS

Platinized platinum electrodes (one made of platinum gauze, the other one a perforated platinum disk) were equilibrated with the solution, and then placed one below and one above the slit.

The absence of a Parker effect (2) is demonstrated by the constancy, within experimental error, of the cell constants. The behavior of slit No. 1 is representative. The cell constants were 269.8 in 0.1 *M* potassium chloride; 272.1 in 0.2 *M* potassium chloride; 270.2 in 0.5 *M* potassium chloride; 271.3 in 1.0 *M* potassium chloride; average, 270.8.

TABLE 1

Specific surface conductivity in 5×10^{-4} *M potassium chloride*

SLIT NO.	CELL CONSTANT	LENGTH	AVERAGE THICKNESS	A.C. RESISTANCE	A.C. SPECIFIC SURFACE CONDUCTIVITY
		cm.	*cm.*	Ω	*mhos*
10	3 344	30.1	0 078	39,000	4.1×10^{-9}
11	11 94	22 6	0.067	108,800	4.3×10^{-9}
8*	71 00	10.6	0.125	600,000	3.6×10^{-9}
7	347 1	8 0	0 180	1,680,000	$4\ 27 \times 10^{-9}$

* The low value for the specific surface conductivity in slit No. 8 is believed to be due to insufficient washing with hot water. Six flasks not treated with hot water gave a value of 3.6×10^{-9} mho with A.C. in 5×10^{-4} *M* potassium chloride.

TABLE 2

Specific surface conductivities at concentrations other than 5×10^{-4} *M potassium chloride*

CONCENTRATION OF KCl	SPECIFIC SURFACE CONDUCTIVITY	
	Slit No. 10	Slit No. 11
M		
1.25×10^{-4}	0.52	0.51
2.5×10^{-4}	0 60	0.53
5.0×10^{-4}	1 00	1 00
1.0×10^{-3}	1.90	1 94
3.0×10^{-3}	4.72	4 97
1.0×10^{-2}	8.80*	

* This value was obtained with slit No. 13.

Hot distilled water was sucked through the slits for several hours before using; they were then equilibrated with solution, by sucking the latter through them for some time. Then the resistance measurements were carried out.

The series was started with 1.25×10^{-4} *M* potassium chloride and ended with 0.1 *M* potassium chloride, unless the Parker effect was being investigated. The slit was then treated with hot distilled water, again equilibrated with 1.25×10^{-4} *M* potassium chloride, and the series repeated. Good agreement was obtained.

As a result of these measurements, we calculate a specific surface conductivity in 5×10^{-4} *M* potassium chloride, of 4.3×10^{-9} mhos. This is a weighted average, based on measurements in four slits. The data are summarized in table 1.

The fraction of the total conductivity contributed by the surface was as follows: slit No. 10, 12.3 per cent; No. 11, 31.6 per cent; No. 8, 37.3 per cent; No. 7, 63.8 per cent. The width of the slits, calculated from cell constants, length, and thickness, is: slit No. 8, 16 μ; No. 10, 8 μ; No. 11, 3 μ; No. 7, 0.6 μ. The fact that specific surface conductivity is independent of the width of the slit (table 1) is noteworthy. This indicates absence of membrane potentials.[2]

TABLE 3

Apparent specific surface conductivities

SLIT NO.	APPARENT D.C. RESISTANCE CORRECTED FOR LEADS	CELL CONSTANT	APPARENT D.C. SPECIFIC SURFACE CONDUCTIVITY
	ohms		*mhos*
10	41,500	3.344	$2\ 2 \times 10^{-9}$
11	128,000	11 935	$2\ 3 \times 10^{-9}$
8*	726,000	71.00	$1\ 9 \times 10^{-9}$
7	3,000,000	347 1	$1\ 3 \times 10^{-9}$

* See footnote to table 1.

The A.C. specific surface conductivities at concentrations other than 5×10^{-4} *M* potassium chloride, are given in table 2, for two slits. The specific surface conductivity in 5×10^{-4} *M* potassium chloride has been selected as reference and assigned the value of unity.

D.C. MEASUREMENTS

The D.C. surface conductivities, calculated from D.C. resistance measurements, may be expected to be lower than the A.C. surface conductivities. This is due to the existence of a counter E.M.F., the membrane potential, which simulates a greater resistance than actually exists.[2]

The polarization to be expected at platinum electrodes was avoided by the use of calomel electrodes of large surface. The E.M.F. used was that of the calomel cell potential difference, or about 3 millivolts. The cells were prepared with 5×10^{-4} *M* potassium chloride.

The slit was placed between the calomel cells, and the deflection of the galvanometer in series was noted. Next the slit was removed, and a known resistance of such magnitude placed in the circuit that the galvanometer deflection was exactly the same as before. The value of this known resistance is the apparent resistance of the slit. These readings could be duplicated several times in succession. The apparent specific surface conductivities were calculated from the apparent resistances, A.C. cell constants being used. The apparent specific surface conductivities are summarized in table 3.

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[2] The membrane potential is defined as a counter E.M.F. which occurs when an electrosmotic current flows through a slit or capillary (1).

The average of the first three values is 2.13 × 10^{-9} mhos, and agrees well, within experimental error, with the value of 2.24 × 10^{-9} mhos found by White, Urban, and van Atta (5) with capillaries having a surface/volume ratio of the same order, i.e., 8000. The low value for the apparent specific surface conductivity in slit No. 7 is due to the extreme narrowness (0.6 μ). The surface volume ratio of this slit is 33,000. The smallest capillary of White, Urban, and van Atta (4) had a surface/volume ratio of about 22,000, and its specific surface conductivity was found to be 1.55 × 10^{-9} mhos.

TABLE 4

"True" D.C. resistances and specific surface conductivities calculated therefrom (5 × 10^{-4} M potassium chloride)

SLIT NO.	A "TRUE" D.C. RESISTANCE	B A C RESISTANCE	C APPARENT D.C. RESISTANCE	SPECIFIC SURFACE CONDUCTIVITY FROM		
				A	B	C
10	38,700	39,000	41,500	4.4 × 10^{-9}	4.1 × 10^{-9}	2.2 × 10^{-9}
11	108,000	108,800	128,000	4.6	4.3	2.3
8*	597,000	600,000	726,000	3.7	3.6	1.9

SLIT NO.	i_1	i_2	E_1	R_1	R_2	LEAD RESISTANCE
	scale divisions	*scale divisions*	*volts*	*ohms*	*ohms*	*ohms*
10	7.45	9.90	0.0015	80,000	50,000	2,500
11	4.1	5.4	0.0015	100,000	50,000	
8*	5.3	5.65	0.0075	50,000	10,000	

* See footnote to table 1.

This falling-off in apparent specific surface conductivity finds its natural explanation in the statement made by Bikerman (1) that the counter E.M.F. (membrane potential) increases with the surface/volume ratio.

DETERMINATION OF "TRUE" D.C. RESISTANCE OF SLITS

The "true" D.C. resistance of the slits was determined by means of an approximate method.

If a small E.M.F. is applied to the slit, through a known resistance, it follows that

$$i_1R_s + i_1R_1 = E - E_{m1} - E_{p1} \qquad (1)$$

where i = current, R_s = resistance of slit, R_1 = known resistance, E = applied E.M.F., E_{m_1} = membrane potential, and E_{p_1} = electrode (polarization) potential. Changing the known resistance to the value R_2:

$$i_2R_s + i_2R_2 = E - E_{m_2} - E_{p_2} \qquad (2)$$

Making the assumption that $E_{m_1} + E_{p_1} \cong E_{m_2} + E_{p_2}$ when the change in i is small, it follows that

$$i_1R_s + i_1R_1 = i_2R_s + i_2R_2 \qquad (3)$$

from which R_s can be calculated when i_1 and i_2 are determined. These quantities are simply proportional to the galvanometer deflections.

The "true" D.C. resistances obtained by this approximation method, and specific surface conductivities calculated therefrom, are given in table 4. For comparison, the A.C. and apparent D.C. values are also included.

DISCUSSION

The agreement between apparent surface conductivities in slits and capillaries, of the same order of surface/volume ratio, indicates that there is no difference in the surface conductivity of fused and fractured glass surfaces, respectively. This conclusion finds further support in the findings of White, Monaghan, and Urban (4) on the influence of electrolyte concentration on the ratio of electrosmotic and electrophoretic mobilities, and of Monaghan and White (3) that ζ-potential is the same at fused and unfused glass surfaces.

Not too much weight should be attached to the "true" D.C. surface conductivity, as the closeness of the approximation is not known. If the "true" surface conductivity can be confirmed by a different method, then the inference would be justified that electrosmose is almost as pronounced with 1000-cycle A.C., as it is with D.C.

SUMMARY

1. Specific surface conductivities of Pyrex slits were determined with 1000-cycle A.C. (1.25×10^{-4} to 1×10^{-2} M potassium chloride) and with D.C. (5×10^{-4} M potassium chloride).

2. The apparent D.C. specific surface conductivity is lower than A.C. surface conductivity. This is due to membrane potentials.

3. The apparent D.C. specific surface conductivity of fractured glass agrees with that obtained previously in smooth capillaries.

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THE INFLUENCE OF ELECTROLYTE CONCENTRATION ON THE RATIO OF ELECTROSMOTIC TO ELECTROPHORETIC MOBILITIES

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Within the past few years it has become evident that the theoretical treatment of electrophoresis and electrosmosis of Helmholtz, Perrin, and von Smoluchowski must be considerably amplified. The expression developed by these authors is as follows:

$$V = \frac{XD\zeta}{4\pi\eta}$$

where V represents either electrophoretic or electrosmotic velocity, X is the applied field, D the dielectric constant, ζ the electrokinetic potential, and η the viscosity of the medium. According to this formulation, the electrophoretic migration velocity of a particle through a given liquid should equal the velocity of flow of the liquid past a fixed surface of the same material as the particle, irrespective of the size or shape of the particle or the nature of the liquid, provided ζ remains constant.

In 1924 Debye and Hückel (10, 16) published a new formula for electrophoretic mobility,

$$V = \frac{XD\zeta}{K\pi\eta}$$

in which K varies as the shape of the particle, having a numerical value of 6 for spherical particles. However, Mooney (19) and Henry (15) pointed out that Debye and Hückel neglected to allow for the distortion of the electric field caused by the particle, a factor which is negligible only when the diameter of the particle $\leqq$ the thickness of the double layer. The von Smoluchowski formula is valid when the ratio of particle diameter to double layer thickness $\geqq$ 600. (Müller (20) misquotes Henry on this point.) For particles of about 1μ diameter the Debye and Hückel formula, according to Henry, should apply in pure water; in solutions more concentrated than $M/100$ the von Smoluchowski formula applies, and in intermediate concentrations the factor K should vary between the limits set by the two formulas, i.e., between 6 and 4 for spherical particles. It will be shown later that under the influence of this effect the factor 6 is approached but never attained.

A second consideration, the distortion of the charge distribution in the double layer caused by the imposed field, may also affect electrophoretic velocity. Müller (20) points out that if the double layer is very thin, the disturbing effect of an applied field of the order of a few volts per centimeter is negligible, since the electric field of the double layer itself is over 1000 volts per centimeter. However, if the double layer is very thick, the outermost ions are in a weak field and hence may be influenced by the external E.M.F. Müller, assuming that this effect is analogous to the retardation of moving ions due to the asymmetrical surrounding field discussed by Debye and Hückel (9), concludes that electrophoretic velocity may be considerably diminished in dilute solutions because of this factor. However, no quantitative expression for this effect on the retardation of electrophoretic velocity is yet available, and indeed Mooney (18) speaks of polarization increasing the velocity of the particle, although this enhancing effect now seems improbable.

Aside from these suggested amplifications of the Helmholtz-Perrin-von Smoluchowski formula, there is the further possibility that the ζ-potential of a small particle may differ from that of a flat surface. This may occur either by a change of charge density or of double layer thickness or of both.

$$\zeta = \frac{4\pi\sigma\lambda}{D}$$

where σ is charge density and λ is the effective thickness of the double layer. Following Müller's treatment in Abramson's paper (4)

$$\lambda = \frac{1}{\kappa}\,\frac{\kappa r}{1 + \kappa r}$$

where κ is a function of ionic concentration and r is the radius of the particle. According to this treatment the double layer thickness will vary significantly with r when $\kappa r \leqq 5$. This predicts a decrease of double layer thickness, of ζ, and of electrophoretic mobility with decreasing radius of particle. It also predicts that with increasing electrolyte concentration "the size effect is shifted to smaller radii or disappears."

The dependence of the adsorbed charge density on the radius of the particle is discussed by Abramson (4). According to his treatment the negative logarithm of the particle velocity should be inversely proportional to the particle radius. It may be pointed out that, unlike the influence of particle radius on double layer thickness, the influence of radius on charge density should operate in all concentrations up to that in which charge density reaches its saturation value, which has been found by Abramson and Müller (7) to be for most materials at about $M/100$ for ions not reversing sign of charge. Since, however, the vapor pressure is increased by only 1 per cent above normal with droplets of 2μ diameter and by only 10 per cent with droplets of $20\text{m}\mu$ diameter, this effect will be negligible with particles in the microscopic range, if the analogy between vapor pressure and solution pressure holds.

From the foregoing considerations it may be predicted (1) that in solutions more concentrated than $M/100$ electrophoretic velocity should be independent of the size and shape of the particle, except for extremely small particles, and should be numerically the same as electrosmotic velocity over a flat surface, and (2) that in solutions less concentrated than $M/100$, electrophoretic velocity may become less than electrosmotic velocity. For a given solution the ratio, R, of electrosmotic velocity to electrophoretic velocity should increase as the radius of the particle decreases; for a given particle size, R should increase as the concentration of the solution decreases. The absolute magnitude of R for a given particle size in a given solution cannot be predicted, but one should be able to demonstrate qualitatively that changes in R take place under the conditions indicated.

Mooney (18) made the first experimental attempt to compare electrophoretic with electrosmotic velocity on the same substance. He found that the mobility of oil droplets in distilled water increased with diameter. The diameter above which no further increase in mobility occurred was established in a later paper (19) as about 100μ. The influence of droplet size on mobility was reduced or abolished by the addition of electrolyte. He compared electrosmotic with electrophoretic velocity in distilled water and in 4×10^{-4} M copper sulfate. In water the velocity of the small droplets was less than that of electrosmosis; that of the larger (about 40μ) was the same as or greater than electrosmosis. The finding of electrophoretic > electrosmotic velocity is, even for the larger particles, probably in error. In the copper sulfate solution the velocities of all droplets were equal and almost as great as that of electrosmosis. Mooney (19) added further data and compared the experimental findings with the limiting slope of his theoretical mobility–diameter curve. In general, he found the expected correlation between mobility and droplet size in the less concentrated solutions, while in the more concentrated solutions droplets of all sizes moved at approximately the same velocity, as predicted. However, a rather wide scattering of the experimental points and the anomalous effects mentioned by Mooney indicated the desirability of similar experiments on a more stable system.

Aside from the work of Mooney there appears to be no direct experimental evidence in support of the theoretical predictions mentioned above. On the contrary, Abramson (4), after reviewing the experimental work of himself and others, concludes that, when the surfaces compared are chemically identical, (1) electrophoretic mobility is independent of particle size, and (2) electrophoretic and electrosmotic velocities are identical. However, a further investigation of the data reviewed by Abramson brings out the fact that in practically every case experimental conditions were such that no size effect would be expected, i.e., either the solutions used were too concentrated or the range in particle size investigated was not sufficiently wide. For example, Abramson (2) found that protein-coated particles of microscopic size have the same migration velocity as the ultra-microscopic protein micelles investigated by Svedberg and Tiselius (23), and Abramson (3, 5) and Dummett and Bowden (11) demonstrated that the migration velocity of protein-covered particles is the same as electrosmotic velocity on a protein-covered surface of zero or small curvature. Since, however, all of these observations were carried out in concentrated solutions (usually $M/50$ buffers) it is evident that no differences in velocity would be expected. The same objection applies to the experiments of Hardy (14) on protein sols in $N/50$ acetic acid, of Abramson (1) on blood platelets and their aggregates in plasma, of Freundlich and Abramson (12) on blood cells and their aggregates in serum, of Prideaux and Howitt (21) on egg albumin in $M/50$ buffer, of Abramson and Michaelis (6) on droplets of Nujol, castor oil, benzyl alcohol, and cocoa butter, bare and protein-covered, in electrolyte solutions, and probably also of Freundlich and Abramson (13) on quartz particles in sugar solutions, since considerable electrolyte must inevitably have been added with the sugar. The observations of McTaggart on gas bubbles (17) in water are confined to bubbles so large (60 to 160μ) that the maximum velocity had probably already been attained by the smallest. Burton's experiments with submicroscopic silver sols (8) are not decisive, since there is little evidence that his variations in methods of preparation actually produced sols of different sizes.

van der Grinten (24), whose data have been recalculated by Abramson (4), found the electrophoretic velocity of small particles of glass in distilled water to be very much less than electrosmotic velocity at a flat surface of the same glass. The value for R, as recalculated by Abramson, varied between 2.2 and 2.8. Abramson, however, dismisses this observation with a suggestion that the surface of a broken glass particle is probably chemically different from a fused or polished surface and hence would not be expected to have the same ζ-potential, and later (5) points to the measurements of Sumner and Henry (22) as evidence that when the glass surfaces are identical, R is practically unity. Sumner and Henry, comparing the electrophoretic velocity of a fused glass cylinder with electrosmotic velocity on a flat glass surface, found an average value for R of 1.14. However, since these experiments were not performed in water, but in 10^{-4}

M phosphate buffer, and the cylinder used was 20μ in diameter and 20 cm. long as compared with particles about 3μ in diameter studied by van der Grinten and by Abramson, it is evidently not necessary to suppose that the fused surface studied by Sumner and Henry was chemically different from the broken surfaces of van der Grinten and of Abramson in order to account for the difference in the value of *R*.

In view of the fact that with the exception of Mooney's work there are no published experiments which furnish even a qualitative test of the late theoretical developments, it seemed desirable to compare the electrophoretic mobility of small particles with electrosmotic velocity on a flat surface of the same material, over a wide range of concentrations, using, in place of the oil emulsion studied by Mooney, solid materials with more stable and easily equilibrated surface properties. It would, of course, be desirable to vary the particle size as well as the concentration, but this introduces great experimental difficulties, and hence has not been attempted in the present work. In the present paper observations on the value of

$$R = \left(\frac{\text{electrosmotic velocity on flat surface}}{\text{electrophoretic velocity of particles 1–3}\mu\text{ in diameter}}\right)$$

for protein surfaces, found by Abramson and others to be close to unity in concentrated solutions, will be extended to more dilute solutions, and those on the value of *R* for glass surfaces, found by van der Grinten and Abramson to be greater than unity in water, will be extended to more concentrated solutions.

EXPERIMENTAL

All experiments were carried out in flat electrophoresis cells of the Northrop-Kunitz type. It has been shown by von Smoluchowski (25) that in such cells true electrophoretic velocity is obtained by observing the particles at 0.211 of the distance from the bottom to the top of the cell. True electrosmotic velocity is the algebraic difference, particle velocity at wall minus particle velocity at 0.211 cell depth from wall, where movements toward anode and cathode are given opposite signs. When no movement occurs at the wall the value of *R* is unity. Since for the purposes of this investigation only the ratio of electrosmotic to electrophoretic velocity was required, the applied field strength was not determined; the voltage drop in any solution was, of course, the same for electrosmosis as for electrophoresis (about 4 volts per centimeter). It was found necessary, in working with unbuffered solutions such as we used, to increase the length of each side arm to about 20 cm. in order to avoid contamination of the cell contents from the electrode reactions. The glass powder was prepared by prolonged grinding of clean Pyrex tubing with a porcelain mortar and pestle. A uniform suspension of any desired particle size can be prepared by fractional sedimentation; in the work reported here the diameter range was from 1 to 3 microns. The cell was illuminated through a dark field condenser and the particles observed through an ocular micrometer. There was no appreciable drift while the circuit was broken. Each recorded velocity is the average of five observations in each direction.

A concentration of 0.01 g. of gelatin per liter was found adequate to coat completely the glass particles, as evidenced by the fact that the isoelectric point of the coated particles was the same as that of the gelatin (pH 4.75). The same concentration is sufficient to coat the cell also (as evidenced by the fact that electrosmosis reverses at the gelatin isoelectric point), if this solution is passed through the cell slowly for approximately an hour. We thus confirm the finding of Abramson (2) and of Dummett and Bowden (11) that this procedure is adequate to insure complete coating. Since this concentration is probably about the minimum which will give a complete coating to the cell in a reasonable time, it was considered better to use 0.1 g. per liter for the present experiments. This solution was passed through the cell slowly for an hour before readings were begun. The salt concentrations investigated were all made up in 0.1 g. per liter gelatin solutions, and each solution remained in contact with both particles and cell for a 15-minute period before observations were begun.

It is necessary that the cell be carefully cleaned in order that normal electrosmosis be exhibited. The criterion adopted of a normal electrokinetic potential at the cell wall was that the electrosmotic velocity in distilled water without protein be at least 2.5 times the electrophoretic velocity with glass particles 1 to 3μ in diameter. In practise, this ratio varied between 2.6 and 3.1,—a range of values which is consistently obtained with proper cleaning. The ratio for gelatin-covered surfaces in distilled water ranged from 1.9 to 2.3. These rather wide variations in the value of R in water and very dilute solutions are probably to be ascribed to differences in electrolyte content of different samples of distilled water, or, in the absence of protein, to variations in the electrical properties of the cell wall, or to both.

Table 1 contains the results of experiments with bare Pyrex surfaces in varying concentrations of potassium chloride. These observations were carried out in a flat Pyrex cell. The sign refers to the pole toward which the particles were moving. Since in potassium chloride the particles are always negatively charged, they move always toward the anode at 0.211 of the distance from the wall. As previously stated, the velocity at this level represents true electrophoretic velocity, V_p. Since, at the bottom of the cell, the particles moved always in the opposite direction if they moved at all, electrosmotic velocity, V_e, is the numerical sum of the observed velocities at the two levels. The absolute magnitude of V_p and V_e

in these experiments is not of quantitative significance, since the field strength may vary slightly from one solution to the next, but the value of R is independent of field strength.

Similar data for gelatin surfaces are given in table 2. No attempt was made to maintain a rigidly constant pH, since the value of R is independent of pH; however, there was no great variation in pH among the different solutions. Table 2 also shows that the same values for electrosmotic velocity are obtained by observing the particles at the wall as by the use of the equation $V_e = 2(V_{\frac{1}{2}} - V_p)$.

Similar observations on both bare glass and gelatin-coated surfaces in contact with thorium chloride are recorded in tables 3 and 4. The tetravalent thorium ion reverses the sign of charge on glass; the isoelectric concentration for electrosmosis and electrophoresis is approximately 3×10^{-6} M. At concentrations near the isoelectric point, the value of R is likely to show irregular variations, but at concentrations other than isoelectric, R approaches unity as the concentration increases.

TABLE 1

Electrophoretic and electrosmotic velocities on bare Pyrex surfaces in potassium chloride

MOLAR KCl CONCENTRATION	μ PER SECOND AT 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+9.7	−16.4	26.1	2.69
5×10^{-5}	+9.9	−11.5	21.4	2.16
5×10^{-4}	+8.5	−5.9	14.4	1.69
1×10^{-3}	+9.0	−4.3	13.3	1.48
1×10^{-2}	+7.9	0	7.9	1.00

Thorium chloride in unbuffered solutions also reverses the sign of charge of gelatin (probably largely a pH effect) at concentrations between 1 and 2×10^{-5} M. Here again the isoelectric point is the same for the particles and the cell, additional evidence that all surfaces are completely coated with protein.

DISCUSSION

The data show that the unqualified statement that electrophoretic velocity equals electrosmotic velocity provided identical surfaces are used is not correct. The equality holds only in relatively concentrated solutions. Conversely, the view that the electrophoretic velocity of unfused bare glass particles must be different from the electrosmotic velocity at a fused flat surface is not correct; the velocities are different in dilute solution (which is also true for protein-covered surfaces) and become the same in relatively concentrated solutions. At a concentration between 10^{-3} and 10^{-2} M the velocities become equal with both bare and protein-covered

TABLE 2

Electrophoretic and electrosmotic velocities on gelatin-coated glass surfaces in potassium chloride + 0.1 g. of gelatin per liter

MOLAR KCl CONCENTRATION	μ PER SECOND AT 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+5.38	−5.50	10.9	2 02
5×10^{-5}	+5.03	−3.79	8 82	1.75
5×10^{-4}	+4.78	−1 47	6.25	1.31
1×10^{-3}	+3.89	−0.81	4 70	1.21
1×10^{-2}	+2.08	0	2 08	1.00

Comparison of two methods for obtaining electrosmotic velocity

MOLAR KCl CONCENTRATION	LEVEL IN CELL	μ PER SECOND	V_p	V_0 AVERAGE TOP AND BOTTOM	V_e $(V_0 - V_p)$	V_e $2(V_{\frac{1}{2}} - V_p)$	V_e AVERAGE	$R = \frac{V_e}{V_p}$
H_2O	Top	−5.74	+7.65	−5.74	13.4	14.9	14 2	1.86
	0 211 from top	+7.94						
	Middle	+15.1						
	0.211 from bottom	+7.36						
	Bottom	−5.74						
10^{-5}	Top	−5.71	+7.98	−5 76	13.7	13.0	13.3	1.67
	0.211 from top	+8.44						
	Middle	+14.5						
	0 211 from bottom	+7.52						
	Bottom	−5.80						
10^{-4}	Top	−4.57	+8.20	−4.90	13.1	12.6	12 85	1.57
	0.211 from top	+8.62						
	Middle	+14 5						
	0.211 from bottom	+7.78						
	Bottom	−5.21						
10^{-3}	Top	–	+6.35	−1.58	7.9	7.3	7.6	1.20
	0.211 from top	+6.43						
	Middle	+10 0						
	0.211 from bottom	+6.27						
	Bottom	−1.58						
10^{-2}	Top	0	+3.52	0	3.52	3.48	3 50	0.99
	0.211 from top	+3.70						
	Middle	+5.26						
	0.211 from bottom	+3.33						
	Bottom	0						

surfaces; at lower concentrations electrosmotic velocity is greater than electrophoretic. The findings are in accord with the theoretical points discussed in the first part of the paper.

We may consider briefly the various factors which might be responsible for the departure from unity of the ratio $\frac{\text{electrosmotic velocity}}{\text{electrophoretic velocity}}$. In the discussion the dielectric constant and viscosity are assigned normal values.

The maximum variation in R, due to variation in K between 4 and 6 as determined by variations in the ratio of particle radius to double layer thickness, could be only between 1 and 1.5, as discussed by Henry (15). Since we have observed R as great as 3.2, this factor alone cannot explain the findings. Moreover, it can be shown that K can never become as great as 6. Henry states that $K = 6$ when double layer thickness, λ, equals particle diameter. However, it is not permissible to substitute $\frac{1}{\kappa}$ for λ when $\kappa r < 5$, according to Müller's treatment (4). Thus, according to Henry, $K = 6$ with a particle of 1μ diameter in pure water, since $\frac{1}{\kappa} = 1\mu$. But according to the equation

$$\lambda = \frac{1}{\kappa}\,\frac{\kappa r}{1 + \kappa r}$$

(r = particle radius), λ is not identical with $\frac{1}{\kappa}$ but equals 3.3×10^{-5} cm.

TABLE 3

Electrophoretic and electrosmotic velocities on Pyrex surfaces in thorium chloride

In this series the long side arms on the electrophoresis cell had not yet been introduced, hence the field strength was greater

MOLAR $ThCl_4$ CONCENTRATION	μ PER SECOND 0.211 FROM BOTTOM $= V_p$	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+16.9	−34.0	50.9	3.01
1×10^{-6}	+14.1	−27.8	41.9	2.99
1×10^{-4}	−21.4	+10.0	31.4	1.47
1×10^{-3}	−28.7	0	28.7	1.00
1×10^{-2}	−23.6	0	23.6	1.00

TABLE 4

Electrophoretic and electrosmotic velocities on gelatin surfaces in thorium chloride + 0.1 g. of gelatin per liter

MOLAR $ThCl_4$ CONCENTRATION	μ PER SECOND 0.211 FROM BOTTOM $= V_p$	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+5.80	−7.60	13.4	2.31
1×10^{-6}	+6.14	−6.26	12.4	2.02
1×10^{-4}	−13.3	+2.9	16.2	1.22
1×10^{-3}	−10.8	+1.7	12.5	1.16
1×10^{-2}	–	0	–	1.00

The condition that λ equals particle diameter can never be attained, since when $\lambda = r$, $\kappa = 0$, i.e., in any solution possessing a finite ionic strength, $\lambda < r$. Thus K must always be less than 6 even with the smallest particles in dilute solutions, although it can become 4 with large particles in more concentrated solutions, and the operation of this effect can vary R only between 1 and something less than 1.5.

This leads to consideration of the effect of particle size on λ, and therefore on ζ and on electrophoretic mobility. According to the equation

$$\lambda = \frac{1}{\kappa}\,\frac{\kappa r}{1 + \kappa r}$$

λ becomes significantly less than its normal value of $\frac{1}{\kappa}$ when $\kappa r \overset{=}{<} 5$. For electrosmosis at flat surface ($r = \infty$), $\lambda = \frac{1}{\kappa}$. Substituting $\frac{1}{\kappa}$ for λ in the condenser equation

$$\zeta = \frac{4\pi\sigma\lambda}{D}$$

(σ = charge density, λ = double layer thickness) for electrosmosis, and $\frac{r}{1 + \kappa r}$ for λ for electrophoresis, it follows that the ratio of electrosmotic to electrophoretic mobilities equals $\frac{1 + \kappa r}{\kappa r}$ or $\frac{1}{\kappa\lambda}$. For distilled water at 25°C., with an estimated ionic strength of 1×10^{-6} and a particle of 1μ radius, $\kappa = 3.25 \times 10^4$, $\kappa r = 3.25$, and the ratio = 1.31. In other words, electrophoretic mobility, *due to the operation of this factor alone,* should be 24 per cent lower than electrosmotic or than the electrophoretic mobility of a particle large enough to escape this effect, or than the electrophoretic mobility of a particle of 1μ radius in a solution strong enough so that $\kappa r >> 5$. In a 5×10^{-5} M potassium chloride solution (ionic strength $= 5 \times 10^{-5}$), $\kappa = 2.3 \times 10^5$, $\kappa r = 23.5$, and the ratio = 1.04. The ratio drops to 1.01 or less, with unity as a limit, in solutions with ionic strength of 5×10^{-4} or greater. In pure water, with a theoretical ionic strength of 1×10^{-7}, $\kappa = 1 \times 10^4$, $\kappa r = 1$, and the ratio becomes 2. It is thus seen that the limiting, and in practise unattainable, value of the ratio for a particle of 1μ radius is 2; for smaller particles the ratio in water of ionic strength 1×10^{-7} could exceed 2. Under the conditions of our experiments the effect of this factor alone is practically negligible with all solutions other than distilled water; with smaller particles the effect should become prominent in solutions of ionic strength[1] greater than 1×10^{-6}.

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[1] A point which seems obscure may be mentioned here. κ is obtained (9) by a series expansion involving

$$\left(e^{-\frac{e\psi}{kt}} - e^{+\frac{e\psi}{kt}}\right)$$

The third factor, the influence of particle size on charge density and therefore on ζ, may be dismissed, since ζ could be changed by only 1 per cent with a particle of 2μ diameter.

The fourth factor, polarization of the double layer, must be invoked to account for the higher values of *R* we have obtained. The maximum combined influence, as seen in water with an estimated ionic strength of 1×10^{-6}, of the first three factors just discussed may be estimated to raise *R* to not more than 2; further retardation of electrophoretic below electrosmotic mobility in water may be ascribed to polarization of the double layer by the impressed field, and this latter factor apparently is the predominant one in any solution of ionic strength greater than 1×10^{-6} with particles as large as 2μ diameter. This is contrary to the suggestion of Mooney (18) that such polarization might enhance mobility. A retarding effect seems to us the more probable.

SUMMARY

The influence of electrolyte concentration of medium on the ratio of electrosmotic to electrophoretic velocities with bare glass and gelatin-covered particles of 1 to 3μ diameter has been investigated. The ratio is unity with either type of surface with a concentration between 10^{-3} and 10^{-2} *M* and at all higher concentrations. With lower concentrations the ratio increases progressively with decreasing concentration, reaching values above 3 in distilled water. A discussion of various factors which may contribute to this result is given.

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where all except the first two terms are neglected, giving $-2\frac{\epsilon\psi}{kt}$. This approximation is justified only when $\frac{\epsilon\psi}{kt} < 1$, which is true only when ψ or $\zeta < 25$ millivolts. Nevertheless, when double layer thickness, λ, is calculated as $\frac{1}{\kappa}$ for 5×10^{-4} *M* potassium chloride at a plane glass surface at 20°C., where $\zeta = 120$ millivolts, a value of $\lambda = 1.47 \times 10^{-6}$ cm. is obtained. We have recently obtained a specific surface conductivity value of 4.27×10^{-9} mhos for 5×10^{-4} *M* potassium chloride at a plane glass surface. From this one finds 1.8×10^{13} ions adsorbed per cm.^{2} of surface. If one substitutes the value of ζ, potential, and σ, electric charge density at surface, corresponding to $\zeta = 120$ millivolts and ions per cm.$^2 = 1.8 \times 10^{13}$, in the condenser equation

$$\lambda = \frac{\zeta D}{4\pi\sigma}$$

one obtains $\lambda = 1.19 \times 10^{-6}$ cm. This is an experimentally obtained value and is subject to no restrictions other than those of experimental error. In view of the above-mentioned restrictions implicit in κ, this correspondence seems surprisingly close.

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A STUDY OF CERTAIN FINELY DIVIDED METALS AND A METHOD FOR THEIR PREPARATION[1]

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INTRODUCTION

More than a century ago attention was directed to the phenomenon of adsorption as an explanation for the phenomenon of catalysis, and the unsaturated forces at solid surfaces were believed to be the real origin of both phenomena. During recent years an intensive study has brought to light the close connection in many cases between catalysis and the specific nature of adsorption (8). In marked contrast to inert adsorbents, metallic catalysts seem to have a definite saturation capacity for certain gases. In the case of the adsorption of hydrogen on nickel this saturation capacity is reached at low pressures (2).

It has been shown that the activity of a catalyst and its adsorptive capacity are greatly affected by the method of its preparation. As it is practically impossible to prepare two catalysts which are exactly alike, it seems very important that adsorption measurements and a study of catalytic activity be made on the same catalyst under the same conditions.

The first work of this nature is that of Pease (5), who has studied the catalytic combination of ethylene and hydrogen on copper by measuring the reaction rate and the adsorption isotherms of the reactants and the product, using the same catalyst for all the measurements. Since then there has been very little work of this kind, although there have been numerous investigations of the adsorption of various gases by several metals which presumably were active catalysts. The metals, which have been used commonly, have been prepared by reducing their oxides with hydrogen.

Metals may be prepared from their amalgams by distilling off the mercury but, so far as the writer is aware, no investigation of the catalytic activity of finely divided metals prepared in this way has been undertaken. Preliminary experiments had shown that metals prepared from the amalgams are active catalysts; therefore it seemed that it would be interesting to study metals prepared in this way.

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[1] From the dissertation submitted by E. G. Insley to the Faculty of Philosophy of The Johns Hopkins University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

The hydrogenation of ethylene was selected as the reaction to investigate in connection with these catalysts, and for several reasons. It is a simple reaction, with no side reactions, and it goes to completion. The reactants and the product are reasonably stable, and the course of the reaction may be followed conveniently by measuring the decrease in pressure, the volume remaining constant.

According to Sabatier (6), the hydrogenation of ethylene occurs at the surface of nickel, cobalt, copper, and iron at temperatures about 150°C. Recently it has been shown that this reaction takes place at a readily measurable rate at 0°C. It was decided to measure the velocity of this reaction at 0°C., and to determine the adsorption isotherms of hydrogen, ethylene, and ethane at 0°C. on each of the above metallic catalysts prepared from their amalgams. Furthermore it seemed that it would be interesting to compare the catalysts prepared from the amalgams with those prepared from the oxides. Accordingly metallic catalysts, prepared by reducing the oxides with hydrogen, were studied in the same manner and under the same conditions as those prepared from the amalgams.

After completing the work outlined above it was decided to measure the adsorption of hydrogen on nickel at higher temperatures.

APPARATUS AND EXPERIMENTAL PROCEDURE

The adsorption apparatus (figure 1) was a modified form of the type of apparatus used by Bennett (1) in the adsorption of carbon dioxide on oxide catalysts. The manifold of the apparatus was connected through a mercury cut-off and a trap to a mercury vapor pump, which was backed by a Hyvac oil pump. The trap was at all times immersed in a bath of solid carbon dioxide and alcohol. The manometers and the cut-off were connected through traps to leveling bulbs. The mercury used for these had been purified by acid washing and distilling in the usual manner.

The bulb B, used to measure the hydrogen admitted to the catalyst, was calibrated, surrounded by a water jacket, and sealed in the system so that it could be connected either to the hydrogen reservoir or to the catalyst in bulb A. A three-way stopcock S was inserted so that gases other than hydrogen could be admitted from a gas buret.

Materials

Recrystallized Baker's C. P. salts were used as the source of the metals. The mercury used in forming the amalgams was prepared by decomposing Baker's C. P. mercuric oxide. The hydrogen used in these experiments was prepared by electrolyzing a 15 per cent solution of sodium hydroxide between nickel electrodes. It was passed through a trap surrounded by solid carbon dioxide to remove most of the water carried over from the generator, then over glowing platinized asbestos to remove traces of oxygen, and finally through a long spiral immersed in liquid air to remove traces of water. It was stored in a 2-liter balloon flask. The ethylene was the compressed gas prepared especially for anesthesia by the Kansas City Oxygen Gas Company of Baltimore. The ethane was obtained from the Matheson Company of East Rutherford, N. J. Both the ethylene and ethane were passed through a long U-tube surrounded by solid carbon dioxide to remove any condensible material. Each of these gases was admitted to the catalyst by means of a water-jacketed gas buret.

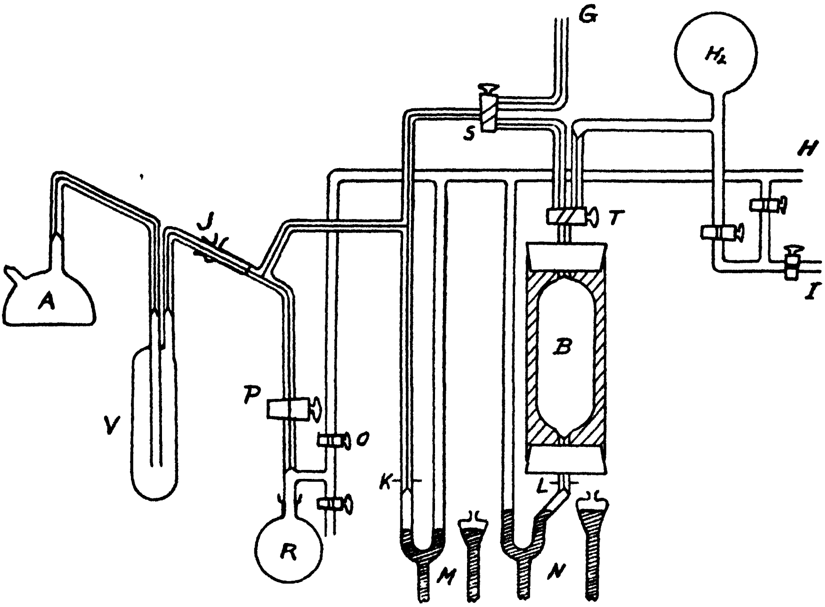

FIG. 1. ADSORPTION APPARATUS
G, to gas buret; H, to high vacuum; I, to hydrogen generator

The metals studied were iron, cobalt, nickel, and copper. Each metal was prepared both from the oxide and the amalgam. The metals prepared from the oxides are referred to as No. 2. Metals referred to by other numbers were prepared from the amalgams. The oxides were reduced in the adsorption bulb by hydrogen for twenty-four hours at the following temperatures: copper No. 2, 200°C.; cobalt No. 2, 390°C.; iron No. 2, 390°C.; nickel No. 2, 275°C.

The amalgams were prepared essentially according to the method given in Smith's *Electrochemistry* for the electrolytic determination of metals using a mercury cathode. About 10 cc. of mercury was put in the cell and connected by a platinum wire in the side arm to the negative side of a

14-volt D. C. line. A solution of the sulfate of the metal, acidified with sulfuric acid, was added to the cell (figure 2), and a platinum anode was then suspended in the solution. In the case of cobalt, iron, and nickel the double ammonium sulfates were used. After the amalgam had been formed, the current was left on, the solution siphoned out, and the amalgam washed with distilled water. Then the amalgam was transferred to the adsorption bulb in the presence of oxygen-free nitrogen, the inlet sealed, and the system evacuated.

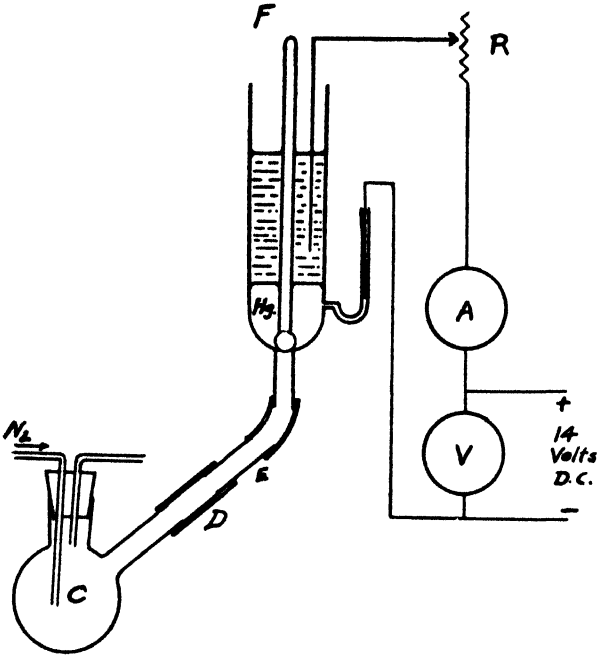

FIG. 2. APPARATUS FOR PREPARING AMALGAM

By means of valve F the amalgam is run into bulb C. Then, closing gum tubing D and removing glass tubing E, the amalgam is transferred to bulb A of the adsorption system. The amalgam is protected by oxygen-free nitrogen.

The capillary tube leading from bulb A (figure 1) was electrically heated by nichrome wire, an electric furnace was placed about bulb A, and the mercury was distilled into trap V. When practically all the mercury had distilled over, the bulb and trap were rotated as a unit about joint J as an axis; the mercury ran down into bulb R. In this way it was possible to remove the mercury from the adsorption system without breaking the vacuum. The last traces of mercury were removed by immersing the trap V in a bath of solid carbon dioxide and ether, and heating the metals to the following temperatures: copper No. 1, 170°C.; cobalt No. 1, 185°C.; iron No. 1, 220°C.; nickels No. 1, 3, and 4, 170°C.; nickel No. 5, 170°C. The evacuation was continued until the pressure became as low as 1×10^{-5} to 1×10^{-6} mm.

Calibration and method of adsorption measurements

With the adsorption bulb empty, the apparatus was evacuated and bulb A was immersed in a bath of finely shaved ice and distilled water. In all experiments the trap V (figure 1) was immersed to the same depth in a bath of solid carbon dioxide and ether. The temperature, as shown by a pentane thermometer, was −81°C. and was kept very nearly constant by adding small quantities of solid carbon dioxide from time to time.

Keeping stopcock P closed and the mercury level in manometer M (figure 1) near the height K, hydrogen was admitted to bulb A from bulb B. Knowing the temperature of the gas, the volume of bulb B, and the change in pressure in bulb B, the volume of hydrogen admitted to bulb A could be readily calculated. After adjusting the mercury level in manometer M to exactly the height K, the pressure M was measured. In the same manner a number of pressures M, corresponding to various quantities of hydrogen, were measured. When these volumes were reduced to 0°C. and 760 mm. pressure and plotted against the pressures, M, a straight line was obtained from which could be read the calibration volume corresponding to any desired pressure.

In an adsorption measurement the volume of gas admitted to the catalyst was corrected for the volume of gas displaced by the metal. This volume was calculated from the known weight and density of the metal. This method of calibration was used by Nikitin (4) in a study of the adsorption of carbon dioxide on metallic iron, cobalt, and nickel. In the case of nickel No. 5 the system was also calibrated using purified helium. The two calibrations checked within 0.01 cc., which is within the experimental error.

After the catalyst had been prepared and evacuated as described above, a small quantity of hydrogen was admitted to the catalyst, the pressure M was measured, and the volume reduced to standard conditions as described in connection with the calibration above. Then by subtracting from this reduced volume the volume of gas required to give the same pressure in the calibration of the system, the volume of gas adsorbed is obtained. By making a series of pressure measurements, M, corresponding to increasing amounts of gas, the adsorption isotherm could be readily determined.

The adsorption at 0°C. of hydrogen, ethylene, and ethane on each metal was measured. In each case, immediately after determining the adsorption of hydrogen on the metal, ethylene was admitted to the catalyst in an amount approximately equal to that of the hydrogen present. Then the rate of hydrogenation was obtained by measuring the rate of decrease in pressure in the system. After evacuating the catalyst, the adsorption of ethylene was measured, and similarly the adsorption of ethane was measured. Before each adsorption measurement, the catalyst was outgassed in the same manner as was used to prepare the metal for the adsorption of hydrogen. In the case of nickels No. 4 and 5 only the adsorption of hydrogen was studied.

In preparing nickel No. 5 the amalgam was evacuated before being heated. After driving off the mercury, the adsorption of hydrogen on the metal was measured at 0°C. Then the nickel was evacuated at 100°C. and the adsorption and desorption of hydrogen at 99.6°C. was measured. Then the metal was evacuated and the adsorption at 0°C. redetermined. After the system had apparently reached equilibrium the bulb containing the metal was slowly heated, keeping the same amount of hydrogen in the system, and pressure measurements were taken at various temperatures up to 150°C. At each of several different points the temperature was kept constant, and pressure measurements were taken until the system had apparently reached equilibrium.

EXPERIMENTAL RESULTS

The larger part of the results will be presented graphically and the corresponding tables omitted. A brief description of the results, obtained from each metal studied, will be given.

Copper. Neither of the catalysts adsorbed a measurable quantity of any of the gases. Copper No. 2 catalyzed the hydrogenation of ethylene at a readily measurable rate (figure 3), but copper No. 1 was completely inactive.

Cobalt. Cobalt No. 2 showed a much higher adsorption of all the gases (figure 4), but both catalysts were equally effective in catalyzing the reaction (figure 5).

Iron. The quantities of gases adsorbed by both catalysts were small (figure 6), the adsorption of ethylene on iron No. 2 being the largest. Iron No. 2 was a much better catalyst for the reaction than iron No. 1 (figure 7).

Nickel. No nickel catalyst prepared from the amalgam adsorbed a measurable amount of any of the gases. Nickel No. 2 adsorbed a comparatively large quantity of hydrogen and ethylene (figure 8). As is shown in figure 9, nickels No. 1, 2, and 3 displayed the same activity in catalyzing the hydrogenation of ethylene.

Nickel No. 5 adsorbed a large amount of hydrogen at 99.6°C. as is shown in figure 10. When the adsorption at 0°C. was repeated it was found to be very small. Keeping the hydrogen, which was admitted at 0°C., in the system and slowly heating the catalyst, it was found that the pressure began to decrease between 50° and 60°C. The measurements at a series of temperatures between −80° and 150°C. are given in table 1 in the order in which they were obtained.

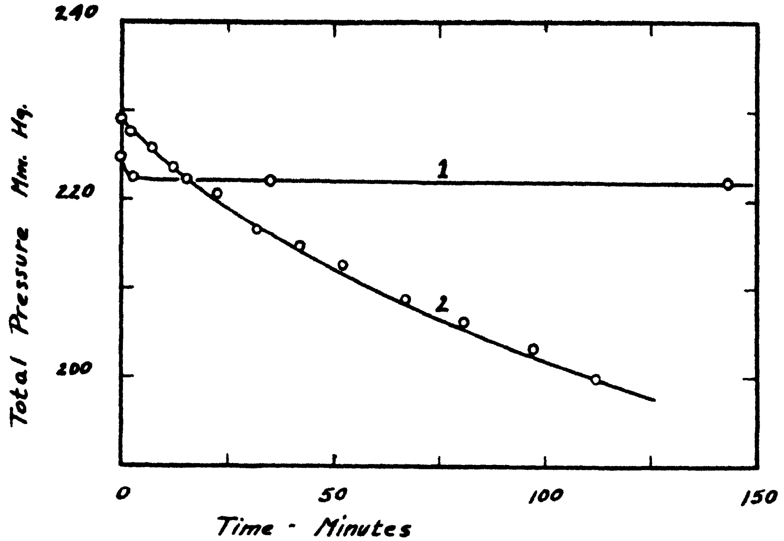

FIG. 3. HYDROGENATION OF ETHYLENE BY COPPER CATALYSTS

Curve 1, copper No. 1 from the amalgam; Curve 2, copper No. 2 from the oxide

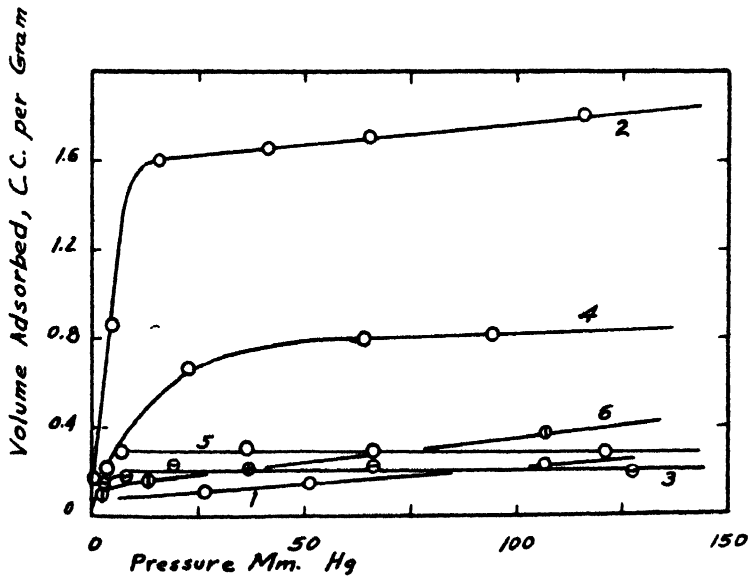

FIG. 4. ADSORPTION BY COBALT CATALYSTS

Cobalt No. 1 prepared from the amalgam; cobalt No. 2 prepared from the oxide. 1, hydrogen on cobalt No. 1; 2, hydrogen on cobalt No. 2; 3, ethylene on cobalt No. 1; 4, ethylene on cobalt No. 2; 5, ethane on cobalt No. 1; 6, ethane on cobalt No. 2.

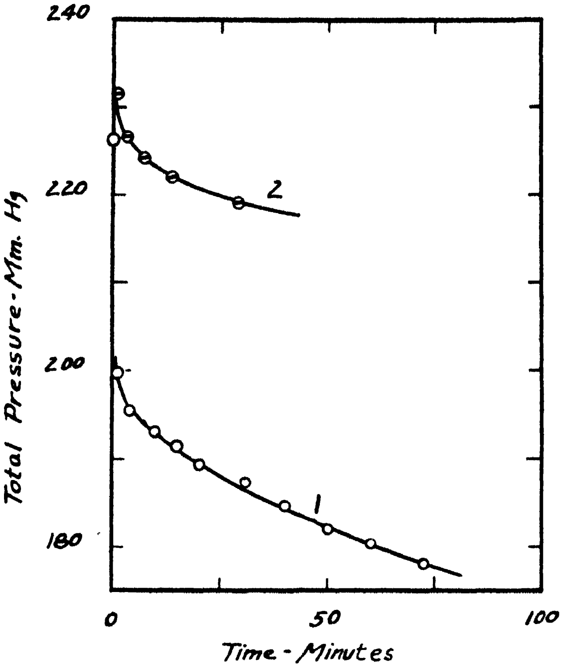

FIG. 5. HYDROGENATION OF ETHYLENE BY COBALT CATALYSTS
1, cobalt No. 1 from the amalgam; 2, cobalt No. 2 from the oxide

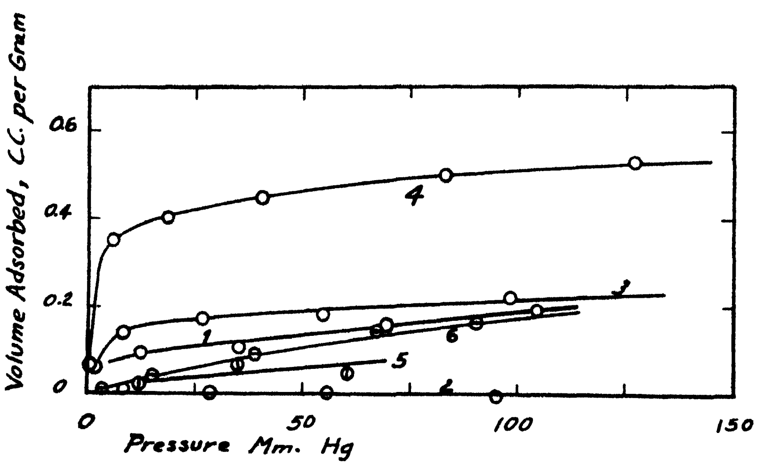

FIG. 6. ADSORPTION BY IRON CATALYSTS
Iron No. 1 from the amalgam; iron No. 2 from the oxide. 1, hydrogen on iron No. 1; 2, hydrogen on iron No. 2; 3, ethylene on iron No. 1; 4, ethylene on iron No. 2; 5, ethane on iron No. 1; 6, ethane on iron No. 2.

DISCUSSION

Adsorption and reaction rates at 0°C.

The adsorption of hydrogen, ethylene, and ethane on the catalysts was in general of the same nature as found by other workers. In the case of the copper catalysts, prepared from both the amalgam and the oxide, and the several nickel catalysts, prepared from the amalgams, the adsorption of the gases was much too small to be accurately measurable. In the case of the other metals studied the amounts of hydrogen and ethylene adsorbed became practically independent of the pressure at fairly low pressures. The amount of ethane adsorbed was approximately proportional to the pressure.

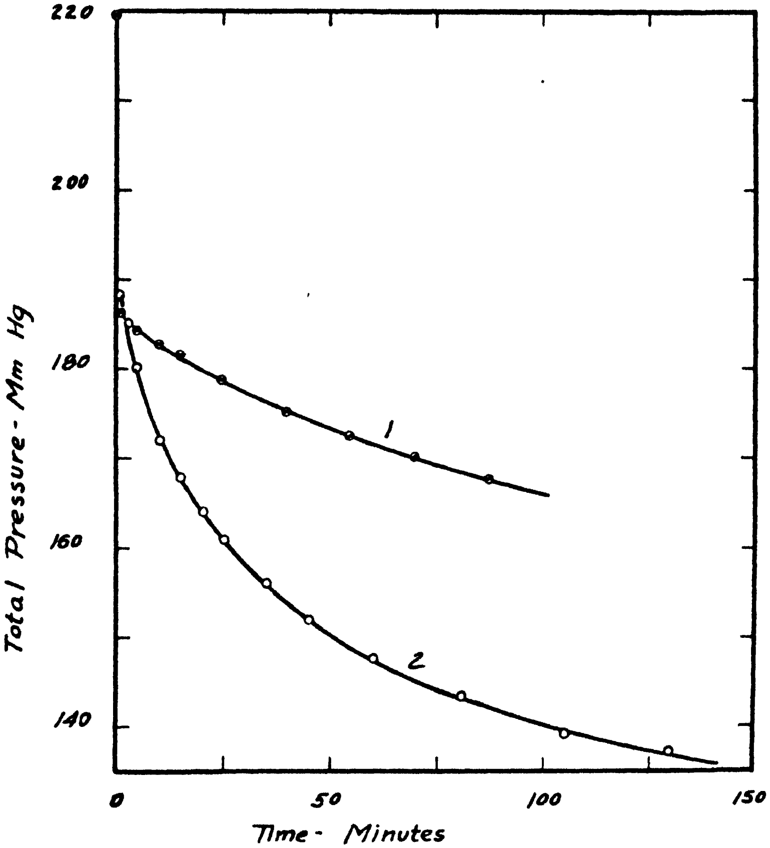

FIG. 7. HYDROGENATION OF ETHYLENE BY IRON CATALYSTS
1, iron No. 1 from the amalgam; 2, iron No. 2 from the oxide

All the metals studied, with the exception of copper No. 1, catalyzed the hydrogenation of ethylene at 0°C. at a readily measurable rate. Copper No. 1 gave practically no reaction even on standing as long as twenty-four hours. This is consistent with the results of Pease (5), who found that mercury poisoned a copper catalyst so that the hydrogenation of ethylene proceeded very slowly and that this poisoning effect was permanent. It

TABLE 1

Adsorption of hydrogen on nickel no. 5

NO.	TEMPERATURE	VOLUME ADSORBED (0°C., 760 mm.)	PRESSURE
	°C.	*cc.*	*mm.*
1	0.0	0.02	20.2
2	72.4	3.15	0.0
3	72.4	3.40	19.9
4	99.5	4.04	15.7
5	150.0	4.06	16.2
6	0.0	4.22	12.3
7	0.0	4.23	12.4
8	−80.0	4 30	10.0
9	99.5	4.16	14.6
10	150.0	4.06	16.2
11	150.0	4.13	57.3

Equilibrium had not been reached when measurements No. 3 and 4 were taken. Between readings 6 and 7 the catalyst was kept at room temperature (26°C.) for twenty-six hours. No. 8, no change in adsorption on standing five hours. No. 10, no change in adsorption on standing ten hours. More hydrogen was admitted between Nos. 2 and 3 and between Nos. 10 and 11.

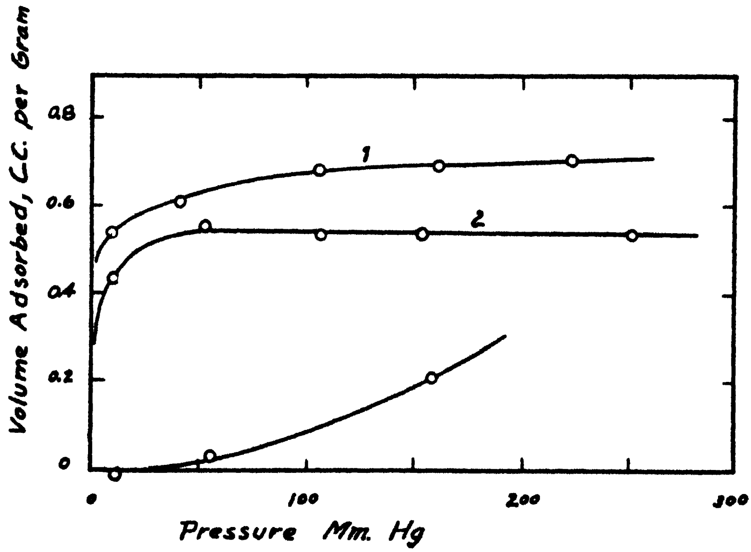

FIG. 8. ADSORPTION BY NICKEL CATALYSTS

Adsorption by nickels No. 1 and 3 (from the amalgam) negligibly small. Adsorption by nickel No. 2 (from the oxide): 1, hydrogen; 2, ethylene; 3, ethane.

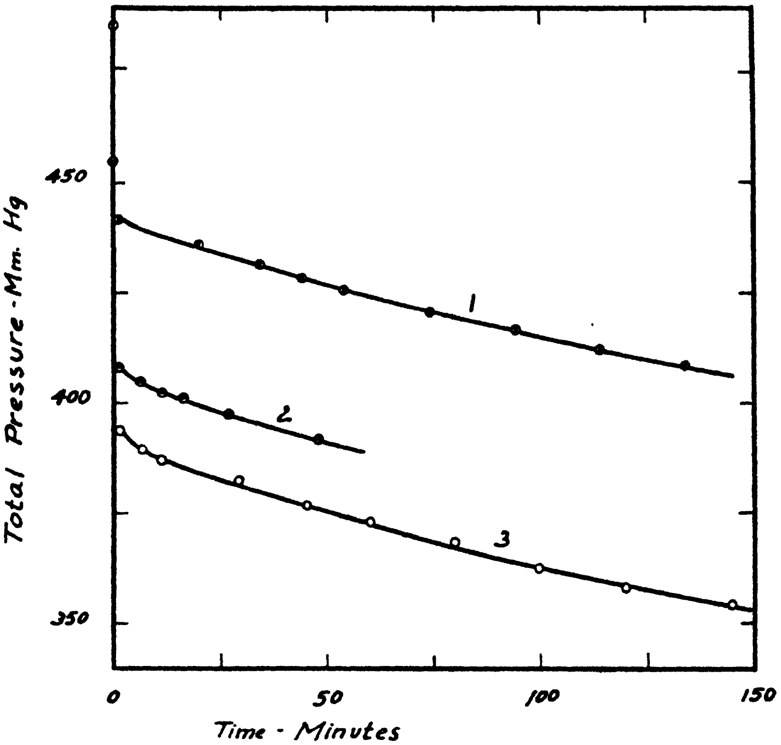

FIG. 9. HYDROGENATION OF ETHYLENE BY NICKEL CATALYSTS

1, nickel No. 1 from the amalgam; 2, nickel No. 3 from the amalgam; 3, nickel No. 2 from the oxide.

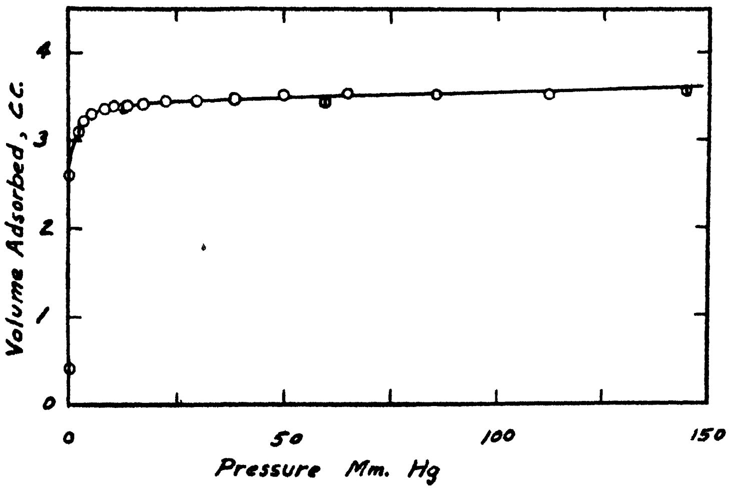

FIG. 10. ADSORPTION OF HYDROGEN ON NICKEL NO. 5 (FROM THE AMALGAM) AT 99.6°C.

⦶, adsorption; ○ desorption

seems that mercury has the effect of destroying the active spots on the catalyst; thus it is not surprising that copper No. 1, prepared from the amalgam, is not an active catalyst. This poisoning effect of mercury was not noticeable in the study of the other metals.

The rate of hydrogenation of ethylene by nickel (figure 9), was the same for the catalysts prepared by the two methods. Both cobalt catalysts (figure 5) gave equally rapid rates of reaction. As nickel and cobalt prepared from the oxides showed much higher adsorption of hydrogen and ethylene than the same metals prepared from the amalgams, it is evident that high adsorption of reactants does not necessarily mean a correspondingly high activity as a catalyst.

The change in total pressure was taken as a measure of the rate of reaction. In the case of iron, nickel, and cobalt from the amalgams, the initial pressures for the reaction rates were calculated from the known volumes of hydrogen and ethylene present and the amounts of the two gases adsorbed. As the quantities of the two gases adsorbed were quite small, it seems that the calculated initial pressures should be fairly accurate. The initial pressures thus calculated are in each of the above-mentioned cases 40 to 60 mm. higher than the first experimentally determined pressure. It is apparent that the initial rate of reaction is very high, for the large decrease in total pressure from its initial value (calculated) to the first experimental value is much too great to be attributed to adsorption, even though the adsorption of the reactants were very high, which is not the case.

Pease (5), in a study of this catalytic reaction, found that when the concentration of hydrogen was kept constant the speed of the reaction decreased as the concentration of ethylene increased. He also found that the deactivation of a copper catalyst by heat treatment or by poisoning resulted in a much larger decrease in the adsorption of hydrogen than of ethylene. This seems to indicate that the adsorption of hydrogen is the more important factor in the hydrogenation of ethylene.

In view of these results an explanation may be offered for the above-mentioned behavior. In all experiments in which the rate of hydrogenation was measured, the adsorption of hydrogen was measured first and then, leaving the hydrogen on the catalyst, an equal volume of ethylene was admitted. Thus at the very first part of the reaction the hydrogen was in large excess. As the ethylene diffused into the catalyst the two gases were competing for the free spaces on the catalyst surface. It seems only reasonable to assume that the amount of hydrogen adsorbed was much greater at the beginning of the reaction than after the gases had become thoroughly mixed. As the reaction rate seems to depend primarily on the amount of hydrogen adsorbed, it seems quite in order that the reaction should be much more rapid at the beginning than after a considerable amount of the adsorbed hydrogen had been displaced by the ethylene.

The above explanation is in agreement with the results of Harker (3), who investigated this same reaction on a supported copper catalyst and found that hydrogen left on the catalyst overnight greatly increased the initial speed of the reaction, while ethylene similarly left on the catalyst greatly reduced the initial speed of the reaction. As Harker has pointed out, the ethylene probably slows down the reaction rate by impeding the movement of adsorbed hydrogen on the catalyst surface to the active centers where the reaction presumably takes place.

The adsorption of hydrogen on nickel at temperatures from −80° to 150°C.

The adsorption of hydrogen on nickel No. 5 (amalgam) at 99.6°C. is very high as compared with the negligibly small adsorption at 0°C. The isotherm (figure 10) shows the adsorption to be completely reversible with respect to pressure.

As is shown by table 1, practically no hydrogen was adsorbed by nickel No. 5 at 0°C., but on slowly heating the catalyst a considerable adsorption began to occur at about 50°C. The adsorption at these temperatures was quite slow; at 72.4°C. more than two hours were required for the system to come to apparent equilibrium. The rate of adsorption seemed to increase with rising temperature. At 100°C. the time necessary to reach apparent equilibrium was less than one hour.

The amount of hydrogen adsorbed was less at 150°C. than at 100°C., and on cooling the catalyst it was found that the amount of adsorbed gas increased steadily down to −80°C. The increase (0.24 cc.) was small in comparison to the total amount adsorbed. On again heating the catalyst the same amount of adsorption was found for each temperature as had been observed at the same temperature in the previous measurement.

From these results it appears that the hydrogen is taken up by the nickel in two ways. The first is ordinary "physical adsorption," which decreases with rising temperature. Numerous measurements had shown the amount of hydrogen adsorbed at 0°C. on this and other nickel catalysts prepared from the amalgam was very small. It was apparent therefore that the amount of "physical adsorption" at 100° to 150°C. was extremely small and practically negligible. The amount of gas taken up in the second manner seems to remain remarkably constant over the range of temperatures studied. The change in adsorption from −80° to 150°C. can be ascribed to the change in the "physical adsorption."

The second manner of "sorption" could be explained by Taylor's (7) theory of "activated adsorption," or by a solution of the gas in the metal or possibly a combination of the two. The time required for the process is in agreement with either explanation. The adsorption isotherm at 100°C. is of the same shape as would be expected on the basis of activated adsorption. However, according to Ward (9), a solution isotherm may have the same form as an adsorption isotherm. The present experimental results do not seem to warrant an attempt to exclude either of these explanations.

SUMMARY

1. The adsorption of hydrogen, ethylene, and ethane has been studied on metallic catalysts prepared from both the oxides and the amalgams.

2. The rate of the hydrogenation of ethylene has been studied on the same catalysts under the same conditions as above.

3. The metals prepared from the amalgams showed a catalytic activity which is quite comparable to that of the metals prepared from the oxides.

4. A very high initial rate of reaction has been found and an explanation has been offered for the same.

5. The adsorption of hydrogen on nickel has been studied at temperatures from −80° to 150°C. It has been shown that only a very small part of the total adsorption is due to "physical adsorption."

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A STUDY OF THE SODA-ALUM SYSTEM. II

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The soda-alum system has been studied by Dobbins and Byrd (2), who determined the 25°C. isotherm and found soda-alum as a stable phase at that temperature. The demonstration of the existence of soda-alum at 25°C. made it seem advisable to continue the investigation further to determine the range of temperature over which it exists as the stable phase. During the progress of the present investigation, Astruc and Mousseron (1) published the data for this system at 5°, 18°, and 42°C., and concluded that soda-alum does not exist below 11°C., nor above 39°C. In the present paper are given the results of a study of the system at 0°, 30°, and 42°C.

EXPERIMENTAL PROCEDURE

Solutions were made, using C.P. sodium sulfate and aluminum sulfate. For each isotherm a series of solutions was prepared containing varying concentrations of aluminum sulfate in contact with solid sodium sulfate, and another series containing varying concentrations of sodium sulfate in contact with solid aluminum sulfate. For the 0° and 30°C. isotherms sodium sulfate decahydrate was used, and for the 42°C. isotherm, anhydrous sodium sulfate was used. The solutions were saturated with the respective salts at temperatures slightly higher than the temperature at which they were to be studied, thus producing equilibrium in a shorter time. Approximately 50 cc. of solution in contact with solid was prepared for each sample, and the bottles placed in the constant temperature bath. The bottles were shaken several times daily, and it was found that equilibrium was reached in less than two weeks. For the 0°C. isotherm, the bottles were kept immersed in a container of crushed ice and water placed in a large refrigerator.

Sampling

After equilibrium was reached, the solutions were allowed to settle completely so that the supernatant liquid was perfectly clear. Samples of the liquid phase were withdrawn by means of pipets and immediately transferred to weighing bottles and weighed. These samples were then diluted to a known volume.

The solid phase presented much difficulty in some cases, owing to the finely divided condition of the solid. In all cases, portions of the solid phase, with adhering liquid, were dipped from the bottles, as much of the liquid as possible was drained off, and the residue transferred to a weighing bottle, weighed, and made up to a known volume.

Methods of analysis

On account of the difficulty of obtaining satisfactory analyses for sulfate in the presence of large amounts of aluminum, it was found advisable to make direct determinations of sodium sulfate and aluminum sulfate. Water was determined by difference.

TABLE 1

0°C. isotherm

SAMPLE NO.	LIQUID		RESIDUE	
	Na_2SO_4	$Al_2(SO_4)_3$	Na_2SO_4	$Al_2(SO_4)_3$
1	6.45	0.00		
2	6.06	3.15	31.44	1.35
3	5.80	5.20		
4	5.55	6.26	29.20	2.36
5	5.40	7.08		
6	5.02	9.33		
7	4.84	9.77		
8	4.70	11.43	31.74	3.71
9	4.38	14.99		
10	4.20	16.47		
11	4.05	19.40		
12	3.85	22.25		
13	2.88	24.23	29.65	8.78
14	2.12	25.55	8.33	39.33
15	1.31	26.42	0.50	44.63
16	0.00	27.97		

Sodium was determined volumetrically by the method of Dobbins and Byrd (3), and aluminum was determined gravimetrically by the method of Dobbins and Sanders (4).

RESULTS

The data for the three isotherms are given in tables 1 to 3 and the results are plotted in figures 1 to 3.

DISCUSSION OF RESULTS

An examination of figure 1 shows that the 0°C. isotherm for this system consists of two solubility curves, with no evidence of compound formation. The composition of the solid phase, determined by means of tie-lines connecting the composition of the liquid phases with the composition of the respective wet residues, shows that the solids in equilibrium with the

TABLE 2

30°C. isotherm

SAMPLE NO	Na_2SO_4	LIQUID $Al_2(SO_4)_3$	RESIDUE	
			Na_2SO_4	$Al_2(SO_4)_3$
1	29.61	0 00		
2	28.10	3.35		
3	27.75	5.14		
4	27 37	6 55	39 20	2 17
5	27 04	8 77		
6	27.00	10.44		
7	26 93	11 42	39.52	3.40
8	26.67	11.73	30.70	11.90
9	24.20	13 55	21 48	19.85
10	15.95	17.73	16 00	24.21
11	12 58	19 49		
13	9.20	22 68		
		25 51		
14	5 43	26.54		
15	5.21	27.20	7.22	29 55
16	3 18	29 56	8.24	32.40
17	2 30	30.87	1 10	44 05
18	1 55	31.21	0 92	42 26
19	0 00	31.99		

TABLE 3

42°C. isotherm

SAMPLE NO.	Na_2SO_4	LIQUID $Al_2(SO_4)_3$	RESIDUE	
			Na_2SO_4	$Al_2(SO_4)_3$
1	32.94	0 00		
2	29.10	6.83		
3	27.13	10 11	75.92	3 86
4	25.70	12 43	76.63	4.07
5	21.12	13.94	20.69	23.77
6	18.74	15.19	18.48	26 31
7	10.31	21.35	12.92	31.45
8	8.03	22.65		
9	5.49	26.94	8 03	31.79
10	2 22	31 32		
11	1.89	32.21	3 26	46.40
12	0 00	34.24		

saturated solutions are sodium sulfate decahydrate and hydrated aluminum sulfate. It is evident that soda-alum does not exist at 0°C.

Figure 2 shows the presence of soda-alum in addition to the two compounds present at 0°C. The limits of concentration between which soda-alum may be prepared are 26.9 per cent sodium sulfate, 11.4 per cent aluminum sulfate, and 4 per cent sodium sulfate, 30.5 per cent aluminum sulfate.

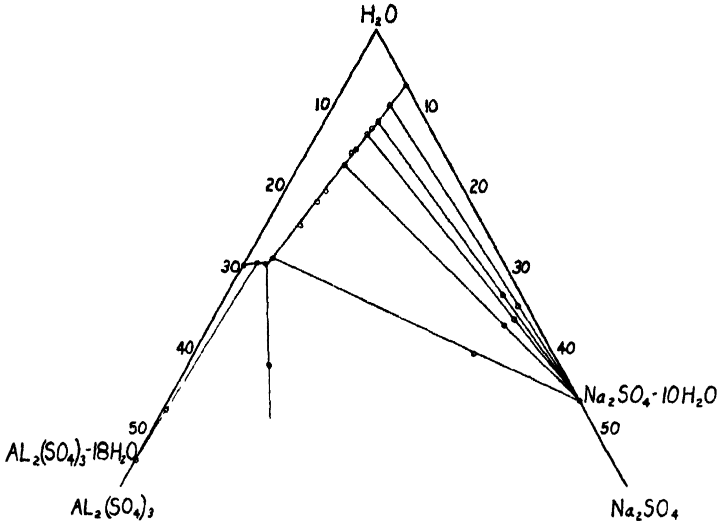

FIG. 1. THE SYSTEM Na_2SO_4–$Al_2(SO_4)_3$–H_2O AT 0°C.

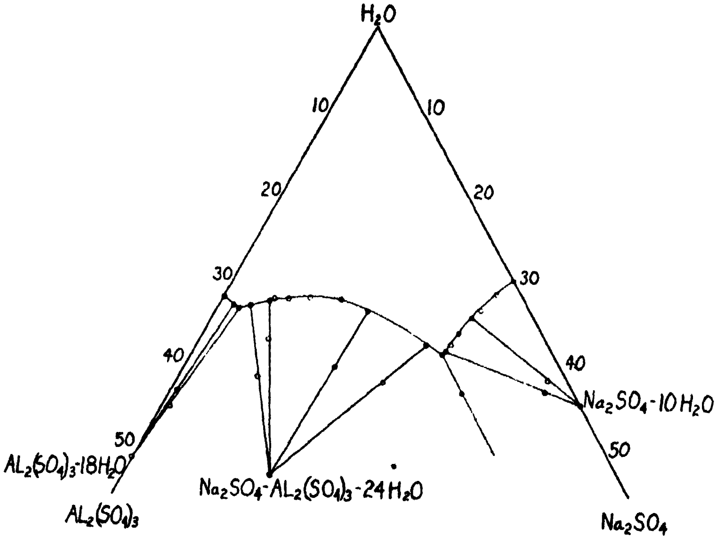

FIG. 2. THE SYSTEM Na_2SO_4–$Al_2(SO_4)_3$–H_2O AT 30°C.

Examination of figure 3 reveals that the 42°C. isotherm is similar to that of the 30°C. isotherm. The solid phases are anhydrous sodium sulfate, hydrated aluminum sulfate, and soda–alum. The determination of the composition of the compound in contact with the middle section of the isotherm presented much difficulty. The solid was very finely divided, and it was impossible to obtain samples comparatively free of the mother liquor. Analysis of the wet residue and extension of the tie-lines to their intersection gave no exact information, since it was impossible to obtain three tie-lines to intersect at one point. Hydrolysis had taken place to some extent, and the excess aluminum present made the intersection of any tie-lines vary greatly from the composition of the alum. The inability to remove the liquid from the residues caused the composition of the residues to be so close to the liquid curve that a small amount of hydrolysis produced a very great effect on the direction of the line.

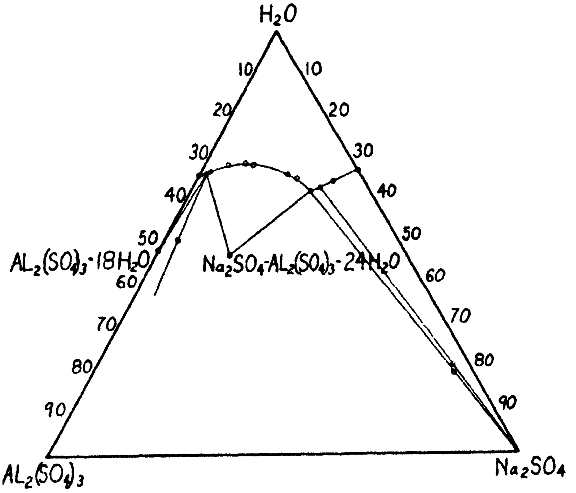

FIG. 3. THE SYSTEM Na_2SO_4–$Al_2(SO_4)_3$–H_2O AT 42°C.

To ascertain the composition of this solid phase, the tell-tale method was used. A small amount of copper nitrate was added to the saturated solutions. Samples of the liquid and the wet residue were taken, and the copper in each was determined electrolytically. From the amounts of copper present, the amount of mother liquor adhering to the solid phase was calculated. Calculations indicated that the solid phase in contact with the middle segment of the 42°C. isotherm consisted of soda-alum with varying excesses of aluminum oxide ranging from 4 per cent to 6 per cent on the extreme left end. On the right portion of this segment of the isotherm, the region of high sodium sulfate concentration, an excess of sodium sulfate was found in the solid. This was most probably due to adsorption.

In order to verify these conclusions as to the composition of the compound in question, a microscopic examination was made of the solid.

This showed conclusively that the substance was composed of small isometric crystals showing the flattened octahedra of the alums.

Since hydrolysis had taken place to some extent, the system should theoretically be treated as a four-component system. However, since the liquid curve is fairly smooth, it is evident that hydrolysis is not a large factor and may be disregarded.

SUMMARY

The 0°, 30° and 42°C. isotherms for the soda–alum system have been determined. There is no alum formation at 0°C. Evidence of the existence of soda–alum as a solid phase at 30°C. and 42°C. was established. Hydrolysis takes place to some extent above 30°C.

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ADSORPTION AND CATALYSIS

J. E. NYROP[1]

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A hot filament of tungsten, iron, molydenum, or platinum placed in vapors of potassium, cesium, or rubidium captures the valency electrons of the atoms surrounding the filament and adsorbs them as ions. The surface thus has ability to cause ionization. By measuring the photoelectric emissivity Brewer (6) showed that the emission curves for iron on which nitrogen, hydrogen, or ammonia has been adsorbed can be duplicated by those obtained from pure iron on which potassium ions have been deposited. This suggests that nitrogen, hydrogen, and ammonia are also adsorbed as ions, and that the strong adsorption on metals, which occurs above certain temperatures, is due to the ability of the surface to cause ionization. As contact catalysis proceeds from the strong adsorption, the ability to cause ionization can be assumed to account for contact catalysis. Coehn and Specht (8) demonstrated that hydrogen adsorbed by palladium is present as ions, since the application of a potential to the metal increases the rate of diffusion of hydrogen to the negative part. This confirms the idea that a metal is able to ionize molecules (atoms) with an ionization potential much higher than the work function of the metal. Since, furthermore, electronic bombardment-synthesis in gas mixtures occurs only when the accelerating voltage is higher than the ionization potential of the molecules most difficult to ionize, and since in the glow discharge it has not been possible to ascribe any reactivity to excited molecules, the mentioned assumption regarding the catalytic effect of the surfaces can be given the following form:—

Postulate I. In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperatures in question able to ionize those molecules among the reactants most difficult to ionize, and the surface will cause a strong adsorption as ions formed are attracted by the surface.

Postulate II. A surface able to ionize molecules of a gas or liquid, and hence able to yield a strong adsorption, produces an increased adsorption when the molecules are substituted by others having a lower ionization potential, assuming all other conditions to be the same.

As to postulate II the variation in adsorption of different gases on a given catalyst is only in the same order as the ionization potential when the ease with which ionization of the molecules takes place and the coefficient of recombination of their ions with electrons are of the same order. Nyrop (17) has calculated the adsorption due to ionization and shown that at a given temperature there is a maximum adsorption and a corresponding saturation pressure. Experiments show that such pressure is a characteristic feature of the strong adsorption in contrast to the van der Waals' adsorption. Nyrop (18) also shows that the positive ion emission from a gas layer adsorbed on a surface having ability to cause ionization is in accordance with the results of Evans (10), and that neutral molecules (atoms) and ions are present on the surface at the same time, since the surface is covered by an electronic gas, the "surface electrons," which is able to neutralize ions formed. The ionization is thus intermittent.

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Savard (23) shows that the energy of dissociation of a molecule A_2 or AB_p is $D_A = 2n(I_m - I_a)$ or $D_{AB} = 2nI_m - n_aI_a$, respectively, when $2n$ is the number of linking electrons in the molecule, n_a the number of electrons in A, I_m the first ionization potential of the molecule, and I_a that of the atom. Ionization of a molecule will thus generally decrease the energy of dissociation and, in the same manner, may be able to reduce the energy of activation of a chemical reaction. The ability of a surface to cause ionization will hence be able to reduce the activation energy of a given process.

It has been observed that there is a considerable difference in the ways in which adsorption takes place on a surface at low temperatures and at high. The low temperature adsorption, being of the van der Waals' type, is instantaneous and without a considerable heat of adsorption, whereas above a certain temperature the adsorption is strengthened and takes place with increasing velocity when the temperature is raised. From the velocity at various temperatures an activation energy can be calculated. Taylor has therefore termed such adsorption "activated adsorption." The heat of adsorption in activated adsorption is higher than in the low temperature adsorption. As the temperature is raised there is at very low temperatures the normal decrease in the van der Waals' adsorption, but, when activated adsorption is possible, such adsorption sets in at a certain temperature, increases with temperature, and passes through a maximum.

Considering ionic adsorption, the ability to cause ionization can be represented by an electric field at the surface, the potential barrier hindering the "free" electrons of the metal in escaping. This barrier, P, retards the "free" electrons having the maximum kinetic energy E and the work function becomes

$$\varphi = P - E \tag{1}$$

If the potential barrier shall be able to ionize molecules coming close to the surface, the potential drop must take place inside a certain distance off the surface, a distance varying with the features of the adsorbed molecules. It shall later be demonstrated that this distance decreases with increasing temperature. The ability to cause ionization is thus enlarged with the temperature, although P may remain constant. P and the distance mentioned are thus determining the ability, and above a certain minimum temperature, T_0, the distance becomes so small that ionization takes place. This is in accordance with the wave mechanics result that the time required for an electron to cross a potential barrier decreases rapidly when the thickness of the barrier is decreased. In this connection the radii of the adsorbed molecules (atoms) have influence, as there may be a certain minimum distance between the nuclei of the molecules and the surface. The ionization power of the surface may thus pass through a maximum when the distance between the surface and the outermost part of the surface electrons is decreased.

That the adsorptive power for lead on platinum, as shown by Maxted (15), is 3.5 times that for mercury confirms postulate II, as the ionization potential of lead is 7.38 and of mercury 10.39 volts. If adsorption and catalysis are considered with heed to the postulates the ability to cause ionization, q_0 (in volts), at a given temperature can be estimated. At the same time T_0 can be determined. Table 1 is a synopsis of such estimates.

By A > B is indicated that the adsorption on the metal A is stronger than on B, or that the energy of activation of a given process is less when A is employed. The ability of A to cause ionization should thus be larger than that of B. When T_0 is lower for the adsorption of a gas on A than on B it indicates that the ionizing ability of A is larger than that of B. Considering the postulates and table 1 we obtain table 2, giving the succession of the metals corresponding to a diminishing ability to cause ionization. The succession of the oxides becomes: $MnO > ZnO > Co_2O_3 > CuO > Fe_2O_3 > V_2O_5 > SiO_2 > Cr_2O_3 > Al_2O_3$.

It will be noticed that the dehydrogenation catalysts are able to ionize hydrogen, and the dehydration catalysts water; and that ammonia is decomposed by the synthetic ammonia catalysts but also by copper able to ionize ammonia and not nitrogen.

There are two types of activated adsorption of hydrogen, for instance, on iron, each type occurring in different temperature ranges. The low temperature activated adsorption may be due to H_2^+ ions, the high temperature to H^+ ions.

According to Sommerfeld (25) the "free" electrons of a metal can be regarded as a degenerate gas capable of expanding. The surface will thus be covered by an electronic gas, the "surface electrons" (17, 18). The "maximum" kinetic energy of the electrons is

$$E = 26\, a^{-2/3}\, n_1^{2/3} \qquad (2)$$

where a is the volume occupied by a gram-atom and n_i the number of "free" electrons per atom. As only few electrons have energies above E this energy is termed the "maximum." When equation 2 is applied and every atom loses one electron ($n_i = 1$), the value E' of table 3 is obtained for the

TABLE 1

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	q_0
			°K.	*volts*
Adsorption of H_2 (I.P. = 15.37 v.)	(7)	Ni	83	>15.37
	(7)	Pt	195	>15.37
	(8)	Fe	90–195	>15.37
	(9)	ZnO	273	>15 37
	(10)	Oxides	>400	>15 37
	(4)	Ni > Pd > Cu		>15.37
Adsorption of N_2 (I.P. = 16 v.)	(8)	Fe	273	>16
	(11)	W	293	>16
	(7)	Ni	98–173	>16
Adsorption of CO (I.P. = 14.4 v.)	(8)	Cu	273	>14.4
	(8)	Fe	195	>14.4
Ethylene (I.P. = 12.2 v.) is adsorbed more strongly than hydrogen (I.P. = 15.37 v.) on Cu, Ni, and Pt, but relatively most on Cu		Ni; Pt > Cu		>15.37
Adsorption of H_2 (I.P. = 15.37 v.) and CH_4 (I.P. = 14.4 v.)	(4)	Cu > C		>15 37
Adsorption of CO (I.P. = 14.4 v.) and H_2 (I.P. = 15.37 v.)	(4)	Ni > Pt > Cu		>15.37
Catalytic exchange of atoms between hydrogen (I.P. = 15.37 v.) and water: $H^2_2 + H_2O \rightleftharpoons H^2_2O + H_2$	(15)	Pt		>15.37
Ortho-para hydrogen conversion	(12)	Fe	83	>15.37
	(13)	ZnO	298	>15.37
	(13)	Al_2O_3	580	>15.37
	(4)	Ni > Cu > C		>15.37
Adsorption of H_2O (I.P. = 12.7 v.) on Hg inhibits photoeffect, H_2 (I.P. = 15.37 v.) does not		Hg		15.37 > Hg > 12.7

TABLE 1—*Continued*

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	φ_0
			°K.	*volts*
Hydrogenation of amylacetylene	(21)			
to amyl acetate to heptane		Cu Ni } Ni > Cu		>15.37
Dehydrogenation of	(22)			
piperidine		Pd > Pt		
cyclohexane		Ni > Os > Pt		
decahydronaphthalene		Ni > Pd > Pt		
Hydrogenation (I.P. = 15.37 v.) of organic products	(4)	Cu; Zn; Ni; Co		
		Ni > Co		>15.37
		Ni > Fe		
Synthesis of acetaldehyde from acetylene (I.P. = 11.2 v.) and water (I.P. = 12.7 v.)		Hg		>12.2
Hydrogenation of C_2H_4 (I.P. = 12.2 v.)	(20) (23)	Pd > Pt > Cu Ni > Co > Zn		>15.37
Synthesis of NH_3 from N_2 (I.P. = 16 v.) and $3H_2$ (I.P. = 15.37 v.)	(4)	Os; Mo; Fe; Ni; Co; Mn; W		>16
		Fe > Pt		>16
		Os > Pt		>16
Decomposition of NH_3 (I.P. = 11.2 v.)	(16) (19)	Cu Os > Pt		>11.2 >11.2
Decomposition of CO (I.P. = 14.4 v.)		Ni > Cu		>14.4
Organic decompositions, etc.		Ni; Co; Fe; Pd, Pt > Cu		
		Ni > Co > Pt; Cu		
Decomposition of ethyl alcohol into aldehyde and hydrogen (dehydrogenation)		Cu; Zn		
Decomposition of ethyl alcohol into ethylene and water (dehydration)		Al_2O_3; W_2O_5		

TABLE 1—*Concluded*

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	φ_0
			°K.	*volts*
By contemporary organic dehydration and dehydrogenation the formation of hydrogen decreases, and that of water increases in the order of the catalysts...	(18)	MnO > ZnO > Fe_2O_3 > SiO_2 > Cr_2O_3 > W_2O_3 > Al_2O_3		
Oxidation of CO............	(14)	Co_2O_3 > CuO > Fe_2O_3 > V_2O_5 > SiO_2		
	(17)	Al_2O_3	<800	
		Cr_2O_3	<700	
		Fe_2O_3	<600	
Oxidation of methanol......		Pt > Cu		
		Ag		
Combustion of a mixture of H_2 and CO................		Pt > Cu		
		Pt > Cu		

maximum kinetic energy. Now some electrons are more loosely bound to the metallic atoms than the rest; hence it is possible that the atoms will lose so many that a stable electronic shell is left. For iron, chromium, manganese, molybdenum, and tungsten, for instance, there are several possibilities; n_i and the corresponding value of E of table 3 is therefore taken as an average when several possibilities are permissible.[2] By measuring the electronic current from a heated metal the work function φ of the table is calculated.

The number of electrons incident on a surface with a kinetic energy of the electron's motion normal to the surface larger than E is

$$n_e = \frac{8\pi m}{h^3}(kT)^2 \tag{3}$$

In a distance s off the surface where the electrons have lost an energy E, these electrons produce a gas with a density

$$n_g = 20\pi(mkT)^{3/2}h^{-3} \tag{4}$$

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[2] In a previous article (17) n_i was estimated without heed to this uncertainty; thus the discrepancy between table 3 and earlier values.

TABLE 2

Succession of the metals corresponding to a diminishing ability to cause ionization

METALS	ABILITY TO CAUSE IONIZATION	IONIZATION POTENTIAL
		volts
Ni	Able to ionize N_2	16
Os		
Fe		
Mn		
Co		
W		
Pd		
Pt		
Zn	Able to ionize H_2	15.37
Cu		
C		
Ag		
Hg	Able to ionize water	12.7

TABLE 3

METAL	φ	E'	z	n_l	E	$E + \psi$
Ni	5.0	7.47	4	4	18.8	23.8
Os		11.60	2	2	18.4	(23.2)*
Fe	4.8	7.15	2–6	4	18.0	22.8
Cr		6.92	2–4–6	4	17.4	(22.1)
Mn		6.77	3–5	4	17.1	(21.8)
Mo	4.6	5.83	4–6	5	17.0	21.6
W	4.5	5.80	4–6	5	16.9	21.4
Pd	4.5	6.40	4	4	16.2	20.7
Co	4.0	7.30	3	3	15.2	19.2
Pt	4.5	5.97	4	4	15.1	19.6
Zn	3.3	5.96	2–6	4	15.0	18.3
Cu	3.7	7.10	1–5	3	14.8	18.5
C	4.1	8.50	2	2	13.5	17.6
Al	3.9	5.63	3	3	11.7	15.6
Au		5.50	1–5	3	11.4	(14.6)
Ag	2.9	5.47	1–5	3	11.3	14.2
Hg		4.42	2–6	4	11.2	(14.0)
Pb	3.9	3.78	4	4	9.5	13.4
Mg	3.0	4.62	2	2	7.3	10.3
Ca	2.2	3.17	2	2	5.0	7.2
Li		3.82	1	1	3.8	(5.8)
Na	1.8	3.14	1	1	3.1	4.9
K	1.2	2.14	1	1	2.1	3.3

* Parentheses indicate that the value has been estimated.

In a zone quite close to the surface and in a distance a off the surface the density is

$$n_a = \frac{8\pi(2m)^{3/2}}{3h^3}(E - E_a)^{3/2} \tag{5}$$

where E_a is the kinetic energy lost by the electrons in moving the distance a. $(E_a < E)$. Near the outermost zone in a distance $x < s$ the density is expressed by an equation similar to equation 4, but the density is somewhat larger. The density of the outermost part of the surface electrons is thus increasing with $T^{3/2}$. Approximately[3] the distance between the outermost zone and the surface, viz., a plane through the exterior nuclei of the metallic ions, is

$$s = 3.6 \times 10^{-6}\, a^{-1/6}\, n_i^{1/3}\; T^{-1/2} \tag{6}$$

and

$$E/s = 7 \times 10^{6}\, a^{-1/2}\, n_i^{1/3}\; T^{1/2} \tag{7}$$

For $T = 100$ we have for silver $E/s = 3.3 \times 10^6$.

As to the field accounting for φ, this is strongest at distances not much larger than s off the surface, but the strength will decrease as the density of the outermost part of the surface electrons is enlarged, i.e., with raising temperature. A part of φ equal to

$$\varphi' = \mu\, T^{-3/2}\, \varphi \tag{8}$$

may thus be able to assist in the ionization. $(\mu\, T^{-3/2}\varphi < \varphi.)$ At high temperatures the maximum ability of a surface to cause ionization is thus equal to E, but at lower temperatures to $E + \varphi'$.

T_0 is the minimum temperature at which the activated adsorption by a given experimental technic is measurable. If T_1 and T_2 are the minimum temperatures for the same gas adsorbed on two surfaces having the ability to cause ionization $E_1 + \varphi_1'$ and $E_2 + \varphi_2'$, we should in accordance with equation 6 have approximately

$$\sqrt{\frac{T_2}{T_1}} = \frac{E_1 + \varphi_1'}{E_2 + \varphi_2'} \tag{9}$$

The adsorption of hydrogen on nickel and platinum mentioned in table 1 gives, when the values of table 3 for E and φ are applied, a minimum temperature for the adsorption on iron of 110°K. Considering equation 9, the minimum temperatures mentioned in table 1 are in agreement with table 3. Further, the succession of the metals of table 2 is the same as that of table 3.

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[3] In calculating s it has been estimated that the electronic density at the surface is equal to that at the interior of the metal, although the density is somewhat less at the surface and just below. The electrons crossing the surface are thus accelerated slightly just before the retardation sets in and $P = (E + \Delta E) + \varphi$.

Taylor suggested that so-called peak areas were associated with special activity. Steacie and Elkin (26) demonstrated, however, that the rate of decomposition of gaseous methyl alcohol over solid and liquid zinc was directly dependent on the temperature, there being no discontinuity at the melting point. It was therefore concluded that the entire surface is uniformly active. A progressive removal of the postulated peak areas by poisoning causes, furthermore, no change in the activation energy of the decomposition of hydrogen peroxide on platinum. It seems thus that the catalytic activity is not bound to certain areas of the surface of a single metal. The ionic adsorption described does not involve any assumption regarding peak areas. A heterogeneous catalyst will, however, have crystal surfaces with different activity.

When ionic adsorption of a gas takes place, the positive ions formed neutralize part of the effect of the surface electrons whereby the distance between the outermost part of the surface electrons and the surface increases, viz., the average field close to the surface is weakened, although the potential difference between any point of the metal and points at some distance from the surface may remain constant. At a certain adsorption the field may thus be weakened to such degree that the surface no more is able to ionize the molecules. The ionic adsorption is hence limited, and molecules with ionization potentials lower than that of the gas will, when admixed, act as poison. Bredig (5) showed that in the decomposition of hydrogen peroxide on platinum, hydrogen sulfide destroyed the activity to a much larger degree than hydrogen cyanide. The ionization potential of hydrogen sulfide is 10.4 and of the cyanide 14.8 volts. Besides the limit of the adsorption set by the weakening of the field, impinging molecules and the presence of the surface electrons counteract the adsorption; the adsorption may thus never reach the limit set by the field. At high temperatures the field is strengthened so much that the influence of the adsorbed positive ions is decreased. Poisons are thus more active at low than at high temperatures; this is a well-established fact. A given reaction may also be self-poisoning. The temperature will therefore have to be above a certain value before the reaction takes place with a considerable velocity. Now the catalysts with high ionizing power are more exposed to poisoning than those with lower. In hydrogenation processes, for instance, platinum and palladium are thus active at room temperature, whereas the more active iron and nickel require a higher temperature. That argon is not as strongly adsorbed as nitrogen although their ionization potentials are of the same order is due to a difference in requirement to the distance over which the potential drop at the surface take place, argon demanding a smaller distance than nitrogen. (Argon has, for instance, a smaller effective sectional area than the nitrogen molecule.)

As mentioned, a too narrow potential barrier in relation to the dimensions of the adsorbed molecules may weaken the power of ionization. In that case a very small concentration of poison will be able to cause an increase in adsorption at lower pressures.

The use of relatively weak catalysts in the hydrogenation of coal, tars, and oils and assisting the hydrogenation by hydrogen sulfide (7), added in the free state or formed *in situ*, may depend on a reaction between the sulfide (I.P. = 10.4 volts) and the organic matters, which in many cases have an ionization potential less than 11 volts. Hydrogen sulfide, on the other hand, poisons, for instance, the reaction between acetylene and water, which takes place on several catalysts, as its ionization potential is lower than that of acetylene (11.2 volts) and water (12.7 volts).

In catalytic hydrogenation of oleic acid the double bond is at low pressures saturated and the carboxyl group is not affected. At high pressure the latter is reduced and the double bond is largely unattacked. The ionization potential of ethylene is 12.2 volts and of carbon monoxide 14.4 volts. It may thus be justifiable to assume that the radicals close to the double bond of oleic acid are more easily ionized than the carboxyl group and are thus hydrogenated preferably at low pressures where the molecules lie flat on the surface. At high pressure, however, the carboxyl group comes more easily into contact with the catalyst, as compression causes the molecules to stand at a fairly steep angle to the surface, hence the preferential hydrogenation of this group. In the hardening of oils, linoleic, linolenic, and other highly unsaturated acids are hydrogenated in preference to oleic acid. When the adsorbed molecules lying flat on the surface are highly unsaturated they are attracted to the surface at two or more points; they are thus adsorbed preferentially to oleic acid having one double bond only. This preferential adsorption is the cause of the preferential hydrogenation.

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THE SOLUBILITY OF LEAD IN MERCURY

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The purpose of this investigation was to determine the solubility of lead in mercury from 20°C. to 70°C., using the general method developed earlier in this laboratory (3, 14), but preliminary work gave indication that special technique and special apparatus would be necessary because liquid lead amalgams oxidize rapidly in the presence of air. Since the free energy of formation of lead oxide from the elements is −41,000 calories (7), this compound would be very stable when once formed.

A critical survey of the existing solubility data for lead–mercury revealed that very little work has been done on this binary system below 100°C. The work of Jänecke (6) extends downward to only 106°C., while Puschin (9) is apparently the only investigator who has reported a series of values below 100°C. However, Puschin's values are few in number, with the precision of these determinations apparently unstated. Hence a careful and precise set of solubility data for lead–mercury at the lower temperatures should be a welcome addition to our knowledge of lead amalgams.

MATERIALS

The lead used in this investigation was from a standard sample prepared by the U. S. Bureau of Standards. The Bureau has quoted no analyses for this material, but its melting point (1) is 327.3°C. as against 327.5°C., the reported value for pure lead (5). Spectrographic analysis of the lead using a Bausch and Lomb Littrow spectrograph indicated that antimony, bismuth, cadmium, copper, iron, magnesium, silicon, and silver were present in amounts varying from a trace as in the case of bismuth, silver, and sodium to faint, very faint, and exceedingly faint quantities with respect to the other elements above mentioned. Calcium was the only impurity found to be present in more than a trace, while titanium and vanadium could not be definitely determined because of the presence of these two elements in the carbon electrodes. It has been concluded therefore, that the impurities present in the lead introduce no appreciable error in the results.

The mercury used was purified by passing it several times through a 5-ft. Meyer column containing 6 N nitric acid and then triple distilling the material according to the method of Hulett and Minchin (4). After this purification, 30-g. samples of this mercury when evaporated in an atmosphere of hydrogen yielded residues averaging 0.2 mg. high in the weighed capsules in which the samples were heated.

APPARATUS

Considerable time and effort were spent in perfecting a solubility tube adapted to the elimination of experimental error due to oxidation of the lead amalgams during any part of the experimental procedure. An illustration of the perfected solubility tube employed in this investigation is given in figure 1. The tubes were made from Pyrex glass. The lead amalgams were prepared *in vacuo* in these solubility tubes by keeping the lead and mercury separated until after each tube had been pumped out. The lead was cut into small cubes, about 2 mm. on an edge, and inserted into the nib A through the open end of the tube B; then mercury was added to the tube by means of a funnel and allowed to collect in the end of the tube at C, after which the tube was sealed up near B. The tube was evacuated through the capillary, D, which was subsequently sealed. The function of the tube E, with its end drawn to a fine tip, was to afford a means of breaking the vacuum in the solubility tube when the amalgam was to be filtered. F indicates the filter section of the tube where the lead amalgam, after passing through glass wool and a fine capillary, was conducted by means of the guiding tube, G, into the receiving section H. After the solubility tube was evacuated, the lead and mercury could be brought together by merely tipping the tube so that the lead would fall out of the nib A into the mixing tube BC.

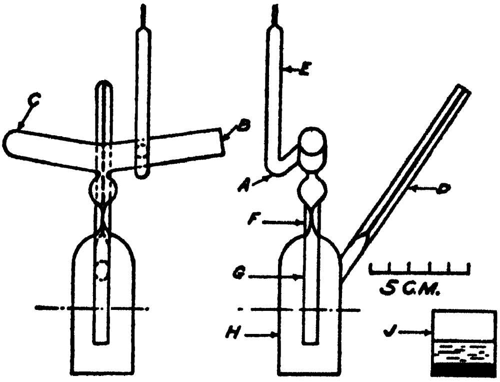

FIG. 1. THE SOLUBILITY TUBE

The thermostat and mechanical equipment used in this investigation were employed previously by other workers in this laboratory (3, 14), and the oven in which the mercury was vaporized in the analysis of the amalgams has also been described (3). The rate of oscillation of the shaking mechanism was adjusted to eleven times per minute to eliminate spattering of the small volume of amalgam in the mixing tube in order that all portions of the mercury should become saturated with lead.

The thermometers employed were of good quality, reading directly to 0.1 and 0.2°C., respectively, and were calibrated against other thermometers certified by the Bureau of Standards. The analytical weights were calibrated by Richards' method and compared with a 10-g. weight certified by the Bureau of Standards.

EXPERIMENTAL PROCEDURE

Before quantitative measurements on solubility were made, the precision of the analytical procedure for lead amalgams was determined. Solubility tubes were cleaned with boiling 6 *N* nitric acid, rinsed with water, and dried in an oven at above 100°C., after which treatment they were charged with a weighed amount of lead, which was placed in the nib A, figure 1, and a weighed amount of mercury, placed in the tube at C. The tubes were then evacuated and sealed at pressures varying from 0.033 to 0.002 mm. as measured by a McLeod gauge, but in a majority of cases the pressure at sealing was not far from 0.01 mm. The data of Puschin were here used to prepare amalgams so that all the lead placed in the tubes would be dissolved.

The solubility tubes were then placed in the thermostat and shaken for several hours, after which the tubes were then rotated through 180° and the amalgams filtered. Filtration was produced by breaking the tip of the tube E, figure 1, to admit purified hydrogen to the previously evacuated solubility tubes, through rubber tubing slipped over the tube E. The sudden change of pressure was sufficient to cause the amalgam to be filtered.

The next step was to analyze the amalgam sample that collected in the receiving part of the tube, H. The analyses were made according to the method of Sunier and Gramkee (12), which consists in the vaporization of the mercury from an amalgam, weighing the residue as the amount of metal dissolved in the mercury.

Special tests have shown that there is less than 0.1 mg. change in weight when 0.3-g. samples of lead are heated in an atmosphere of hydrogen to above 440°C. for at least eight hours.

The experiments summarized in the data of tables 1 and 2 indicate that the average deviation of the analytical concentration from the known value was 2 parts per thousand or below, and that this analytical method is entirely adequate for the analysis of lead amalgams having concentrations of the order studied in this investigation.

The precautions to be taken during the analysis of lead amalgams by this method are (1) protection of the amalgam from oxidation at all times, and (2) heating the lead amalgam during the process of vaporization of mercury from it to not over 350°C., so that bumping of the amalgam may be eliminated.

Details of the handling of the amalgam after filtration were as follows: (1) the entire solubility tube with contents was weighed; (2) the solubility tube was opened by a hot glass rod applied to a file mark along the dashed line as in figure 1; (3) the amalgam in the lower part of the tube was covered with benzene (figure 1 J) and then placed in the oven for vaporization of mercury from the amalgam; (4) the part of the solubility tube above the dashed line was weighed on the analytical balances to the nearest milligram; (5) the lower section of the tube with its residue of lead was removed from the oven and weighed; (6) afterwards the lead was quantitatively removed by dilute boiling nitric acid, and the emptied tube was dried and

TABLE 1

The solubility of lead in mercury

TUBE	LEAD TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION IN PARTS PER THOUSAND
	grams	*grams*			
1	0.2577	36.057	0.6872	0.6874	0.3
2	0.2593	37.524	0.6646	0.6672	3.9
3	0.2580	34.807	0.7125	0.7139	1.9
4	0.2569	35.727	0.6914	0.6931	2.5
Average			0.6889	0.6904	2.2
Deviation of average composition					2.2

TABLE 2

The solubility of lead in mercury

TUBE	LEAD TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION IN PARTS PER THOUSAND
	grams	*grams*			
1	0.6041	28.575	2.006	2.006	0.0
2	0.6093	27.892	2.071	2.071	0.0
3	0.6097	28.569	2.025	2.019	3.0
4	0.6079	29.363	1.965	1.966	0.5
Average			2.017	2.016	0.9
Deviation of average composition					0.5

weighed empty. The difference between the value of operations No. 1 and No. 4 determined the weight of the lower part of the tube, J, plus the weight of the amalgam taken. Operation No. 3 was for the purpose of protecting the lead amalgam from the air until the tube was placed in the oven in an atmosphere of hydrogen. From the measurements outlined above, the atomic per cent of lead in the amalgam was calculable, and it is seen from this description that the easily oxidized amalgams were exposed to oxygen for only a few seconds, from the time the hydrogen-containing solubility tubes were opened until the amalgams in the lower sections were covered with benzene. It is to be pointed out here that the analyses reported in table 1 were made using a somewhat different type of tube than the perfected apparatus, and that the results in table 2, excepting tube 4, were obtained using a tube differing from the one illustrated, in that a small crucible was sealed inside of the tube H. However, it is believed that the high precision of the blank analyses, as well as the precise results in subsequent solubility determinations using the solubility tube shown in figure 1, are proof enough of the validity of the analytical method and of the efficacy of this type of tube.

The procedure when measurements of the solubility at a given temperature were to be made differed from the procedure in the study of the analytical method in that there was at least a 100 per cent excess of lead present in the mixing tube, using Puschin's data as a guide. The earlier runs appeared to indicate that the attainment of equilibrium was rather slow when the amalgam, at a given temperature, was nearly saturated with lead. For that reason, practically all of the runs were made at constant temperature for a considerable length of time, necessitating for practical reasons that equilibrium be approached, for a given run, from one side only.

EXPERIMENTAL RESULTS

In table 3 are presented complete data for a typical run, while table 4 gives a summary of data for all runs. Because there was some duplication of determinations at various temperatures, it seems desirable that the more accurate and reliable data should be indicated, and the mean probable error for each group of such determinations stated. This information has been compiled in table 5. In the calculation of atomic percentage, 200.61 was used for the atomic weight of mercury and 207.20 for the atomic weight of lead.

DISCUSSION OF RESULTS

Criteria which were employed in the selection of the best data were (1) length of run, (2) temperature control, (3) number of determinations, and (4) the precision of the various measurements. As has been previously indicated, the attainment of equilibrium was found to be moderately slow,

—much slower in fact than was found to be true in the determinations of gold solubility in mercury by other workers in this laboratory (12, 13, 14).

TABLE 3

Complete data for run J

Time of run, 115 hours; equilibrium from the low side; temperature, 39.9°C.

TUBE	WEIGHT OF LEAD	WEIGHT OF AMALGAM	ATOMIC PER CENT LEAD	DEVIATION FROM MEAN IN PARTS PER THOUSAND	REMARKS
	grams	*grams*			
1	0.5277	23.214	2.203	0	
2	0.6090	26.769	2.204	0.5	
3	0.6051	26.363	2.224	x	Exclude
4	0.5391	23.737	2.201	0.9	
5	0.6495	28.511	2.207	1.8	
6	0.5847	25.700	2.204	0.5	
7	0.5926	26.092	2.201	0.9	
8	0.6216	27.394	2.199	1.8	
Average..............................			2.203 ±.001	0.8	

TABLE 4

Summary of solubility data for all runs

RUN	TEMPERATURE	ATOMIC PER CENT LEAD	DEVIATION IN PARTS PER THOUSAND	NUMBER OF TUBES	TIME
	°*C.*				*hours*
AA	16.1†	1.372	30	4	8
M	19.7	1.469	11	8	286
K	30.7	1.811	2	8	120
J	39.9	2.203	1	7	115
A	46.5†	2.509	2	3	5
D	47.4	2.592	7	5	22
C	47.4	2.559	11	5	8
B	47.4	2.567	4	3	29
H	48.2	2.631	1	7	115
E	60.5	3.425	2	3	41
F	60.6*	3.438	2	5	34
L	69.2	4.279	4	6	203
G	70.2	4.340	5	3	23

* Equilibrium approached from both sides.

† Uncalibrated thermometers used in these two runs.

Hence no run was considered to be reliable in which the time of the run was less than twenty-two hours. In all of the accepted runs the temperature was automatically controlled by a mercury thermoregulator of the type employed by Clark (2) and constant temperatures within 0.01° and 0.02°C. limits could be maintained over a period of days, and to within 0.005°C. over a period of hours. No run was included among the selected data unless the total number of acceptable determinations was at least five, and exclusion of doubtful or wild values was made on the principle that many small variations occur with higher frequency than do larger variations from the mean, and the general criterion for elimination of values having large deviations was followed (8, 11).

In table 5 the mean for the B and D determinations has been presented because the two runs were made at the same temperature within the limits of experimental error, and the runs were made for nearly the same length of time. Moreover an average of many determinations under practically identical conditions should be more reliable than the two sets of values reported separately, because the value of a mean determination increases with the number of precise observations.

TABLE 5

Summary of best data on solubility

RUN	TEMPERATURE	MEAN VALUE ATOMIC PER CENT LEAD	MEAN PROBABLE ERROR	PROBABLE ERROR OF SINGLE DETERMINATION	NUMBER OF DETERMINATIONS
	°C.		± *per cent*	± *per cent*	
M	19.7	1.469	0.005	0.013	8
K	30.7	1.811	0.001	0.003	8
J	39.9	2.203	0.001	0.002	7
B	47.4	2.588	0.005	0.012	7
D					
H	48.2	2.631	0.001	0.003	7
F	60.6	3.438	0.003	0.006	5
L	69.2	4.279	0.006	0.015	6

The solubility curve (see figure 2), log N_{Pb} versus $1000/T$, was drawn in such a manner that the most reliable values were given the greater weight, with the line of the curve following the more precise observations more closely than the observations whose accuracy and precision, for one reason or another, were regarded as the less reliable. The dotted line in the graph is that drawn for Puschin's data, and was made with due regard for other values from his work which lie beyond the scale of this graph.

In table 6 the solubility of lead in mercury at rounded temperatures as read from the log N_{Pb} versus $1000/T$ plot is presented. The equation for the solubility versus temperature curve, between the limits 19.7°C. and 69.2°C., is

$$N_{\text{Pb}} = 0.5893 - 0.004115T + 0.000007354T^2$$

where N_{Pb} is the atomic fraction of lead dissolved and T is the absolute temperature. The equation was calculated by least squares from the data in table 5, and is useful for determining solubility with moderate accuracy, but for the closest estimation the use of a large plot of the data is recommended.

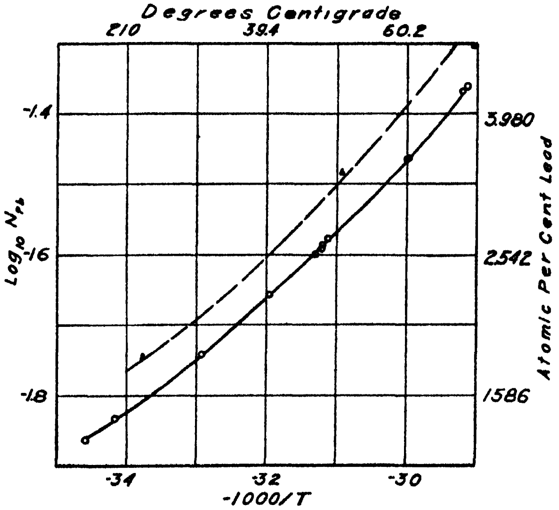

FIG. 2. LOG N VERSUS 1000/T PLOT
△, results of Puschin; ○, results of author

TABLE 6

Solubility of lead in mercury at rounded temperatures

(From log N versus 1000/T plot)

TEMPERATURE	ATOMIC PER CENT LEAD (FROM CURVE)	ATOMIC PER CENT LEAD (CALCULATED)	ERROR IN PARTS PER THOUSAND
°C.			
20	1.476	1.50	16
30	1.780	1.76	11
40	2 199	2.18	9
50	2.742	2.74	1
60	3.419	3.46	12
70	4.330	4.31	5

Examination of the curve shows that the author's data give lower values for the solubility than those of Puschin for corresponding temperatures. This may be due to the fact that in making a solubility curve for amalgams, using a thermal method as Puschin did, supercooling, particularly at lower temperatures, might be more apt to occur, yielding high values for the solubility. On the other hand, it is difficult to conceive how the author's data can be much lower than the true value, because such an extraordinary length of time has been allowed for equilibrium to be attained. There is no evidence to indicate that lead amalgams are colloidal in character within the concentrations studied, if the high precision of the determinations may be used as a criterion of homogeneity.

The curvature apparent in the log N_{Pb} versus $1000/T$ plot, instead of the straight line which is obtained when there is strict conformation to Raoult's law, may be due to the fact that the solid phase is not the one indicated, or to the fact that the latent heat of fusion of lead is some unknown function of the temperature and cannot be considered as constant. No tests have been made in this study to determine the nature of the solid phase in equilibrium with the liquid solution, but Puschin (9), after reviewing previous work, presents evidence of his own to indicate that solid solution is the solid phase.

In a paper by Richards and Garrod-Thomas (10) on electrochemical measurements of amalgams, it is stated that a 1.02 per cent lead amalgam by weight, corresponding to 0.997 atomic per cent, is an unsaturated amalgam at 0°C. Extrapolation of the author's curve verifies this statement, and indicates the saturation value to be 1.072 atomic per cent lead at 0°C.

SUMMARY

1. Special solubility apparatus has been designed and special experimental technique developed for the efficient handling of the rapidly oxidized lead amalgams. This type of apparatus and technique may be of use also in studies of other easily oxidized amalgams.

2. About seventy determinations of the solubility of lead in mercury have been made in the temperature range 20°C. to 70°C., with an average deviation of about 5 parts per 1000 for the final runs.

3. The experimental results are adequately represented by the following equation within the temperature range studied:

$$N_{\mathrm{Pb}} = 0.5893 - 0.004115T + 0.000007354T^2$$

To Professor Arthur A. Sunier the author is indebted for counsel and assistance, and to the University of Rochester for making this research possible. The author is also indebted to Mr. T. J. Zak of the Bausch and Lomb Optical Company for the spectrographic analysis of the lead from the Bureau of Standards.

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PHYSICAL CHEMISTRY OF THE PROTEINS IN NON-AQUEOUS AND MIXED SOLVENTS. II

ELECTROCHEMICAL PROPERTIES OF PROTEIN SOLUTIONS IN CERTAIN GLACIAL ORGANIC ACIDS

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INTRODUCTION

In general the proteins are insoluble in the most commonly used organic solvents, but there are known a few anhydrous and a larger number of mixed solvents which will dissolve many of the proteins. These solvents consist largely of a number of alcohols and hydroxy compounds, some aliphatic carbon acids, and certain not very closely related nitrogen compounds. The separation of the prolamines by alcohol mixtures is the best example of the use of a mixed solvent in protein chemistry.

In the first paper of this series a study was made of the state of aggregation of certain proteins in mixtures of urea and water and of glycerol and water (1). In this communication there will be presented the results of experiments on the electrochemical properties of protein solutions in the aliphatic carbon acids, formic, acetic, and lactic.

GLACIAL ALIPHATIC CARBON ACIDS THAT ARE PROTEIN SOLVENTS

Formic, acetic, lactic, and pyruvic acids have been reported to be solvents for proteins. The earlier literature of the subject contains the information that gelatin dissolves in glacial acetic and lactic acids (see ref. 12), that Mathewson (13) prepared solutions of gliadin in glacial acetic acid, and that Robertson (16) found that casein would dissolve in anhydrous formic acid with ease. A more systematic survey of the subject has recently been published by Loiseleur (10). In the course of the present work, most of Loiseleur's observations were confirmed, but in a few instances there was a disagreement with his statements. With Loiseleur, it was observed that anhydrous formic acid readily dissolves most proteins in the cold, including such diverse members as gelatin, casein, fibrin, edestin, gliadin, egg albumen, zein, etc. Apparently the only proteins not dissolved are certain of the keratins.

Loiseleur states that acetic acid dissolves gelatin in the cold and edestin on heating, but does not dissolve the other mentioned proteins. The only dry protein we were able to dissolve in acetic acid was gelatin, and in the course of this there was noted the paradox that solutions could be prepared and were stable when the gelatin concentration was above a certain critical value, but that it could not be brought into solution in concentrations below this critical level (9). Attempts to dissolve edestin in acetic acid were unsuccessful even after prolonged heating on a water bath.

According to Loiseleur, propionic acid dissolves none of the proteins, but the substituted propionic acids, lactic and pyruvic, readily dissolve many proteins. In our experience casein and edestin swell and slowly go into solution in lactic acid at room temperature. Heating markedly accelerates the rate of solution. Shreds of fibrin become hugely swollen in cold lactic acid, but only on being heated do they completely disperse.

Loiseleur emphasizes the point that protein solutions in the organic acids do not have the usual properties characteristic of colloidal solutions in water. They are not turbid, do not foam, have a low viscosity, and are not coagulated by the protein precipitant acids, tannic, trichloroacetic, and picric, nor by salts of such heavy metals as iron, chromium, and lead. However, by merely diluting these organic acid protein solutions with water, the characteristic colloidal properties are at once restored.

Because of these effects, Loiseleur takes the point of view that in the anhydrous solutions the proteins are actually in "true" solution. Just what is implied by this is somewhat ambiguous, since no further elaboration of the author's conception of the distinction between true and colloidal solutions is given. We assume it is implied that these acid solvents cause a disaggregation of the proteins into units of low molecular weight, since it is generally accepted that colloidal properties are associated with a high molecular size. If this hypothesis is correct, and it were possible to demonstrate that the proteins disaggregate into small units in any group of solvents, it is readily seen that it would be a matter of great importance for chemical theories of the structure of the proteins. One class of substances, namely the soaps, is known to exist as aggregated colloidal micelles in aqueous solution and as simple molecules in alcoholic solution (11). If we interpret Loiseleur correctly, he views the change of properties from aqueous protein solutions to those in the glacial acids as a similar transformation. This conception is not completely novel. Similar suggestions have been proposed, for example, by Herzog and Kobel (7) and by Troensegaard and Schmidt (21). Experimental evidence for such a transformation was offered in what was supposed to be the low molecular weight, 200 to 600, obtained by freezing point measurements of proteins in phenol solution. However, Cohn and Conant (4), who reëxamined the question, showed that the above measurements actually were in error owing to the traces of moisture which were introduced with the protein samples. When this error is eliminated, no disaggregation of proteins in liquid phenol can be demonstrated.

The claim that proteins dissolved in the aliphatic carbon acids lose all of their colloidal properties, moreover, is not completely correct. Concentrated solutions of casein in formic acid, dissolved by heating, set to gels on cooling, and these solutions also show a distinct turbidity. One of the colloidal precipitants, phosphotungstic acid, is able to precipitate proteins even from formic acid. Moreover, the lack of the properties usually associated with colloidal solutions is not a sufficient criterion for invariably assuming a change in the state of aggregation. A similar lack of colloidal properties is found with protein solutions in concentrated urea, which also show no turbidity, do not foam, and are not coagulated by heat. Yet, as was shown by Burk and Greenberg (1) and by Burk (2), many of the proteins have the same molecular size in urea as they do in aqueous solution.

The experiments reported here were undertaken because of their interest to the subject of the structure and the physicochemical state of the proteins, and also for their significance to theories of solubility. Since most of the solvent mixtures for proteins are weak acids or bases, it has been proposed that the solvent properties depend upon the formation of electrically charged protein ions by the interaction with the solvent acid or base. This is undoubtedly the case in many instances, but is by no means universally true. Burk and Greenberg have shown that urea does not act as a protein solvent because of basic properties, and in this communication it will be shown that the same is true of certain of the glacial acids.

EXPERIMENTAL

The conductivities were measured by the Kohlrausch telephone method, using a General Radio Company oscillator as the alternating current source. The semi-micro cell of 2.5 ml. volume shown in figure 1 was employed in all the measurements. An interesting feature of the cell, aside from its size, is that the electrodes, indicated by "s" in the drawing, were formed by spiraling 22 gauge platinum wire. These electrodes were coated with platinum black electrolytically, and the cell constant was determined against standard solutions of potassium chloride in the usual manner. The solvent materials used for preparing the solutions were as follows: Kahlbaum's 100 per cent formic acid, specific conductance about 10^{-4} mhos; Baker or Merck's 85 per cent glacial lactic acid[1] with a conductance of around 5×10^{-5} mhos; and Baker's 99.5 per cent glacial acetic acid with a conductance of less than 10^{-7} mhos.

The proteins used were purified preparations of low ash content. Casein was prepared by the method of Van Slyke and Baker (22), edestin by that of Osborne (14). The gelatin was an Eastman Kodak Company's electrolytically deashed preparation, and deaminized gelatin was prepared from this as described by Hitchcock (8).

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[1] Completely anhydrous lactic acid cannot be used for solvent purposes, as it is a crystalline solid at ordinary temperatures.

All of the protein concentrations are recorded in the tables on the basis of grams of dry protein per liter of solvent. Wherever necessary for this purpose, a correction has been applied for the moisture content of the protein.

Conductivity measurements

The conductivity data obtained in this investigation are recorded in tables 1 to 5. The observations in glacial lactic and acetic acid, which are given in table 1, may well be considered together, separately from the results in formic acid.

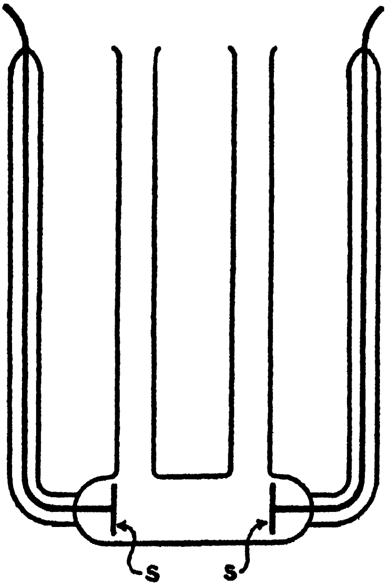

FIG. 1. SEMI-MICRO CONDUCTIVITY CELL

The three proteins, casein, edestin, and gelatin, as noted in table 1, add practically nothing to the conductance of glacial lactic acid. In acetic acid, gelatin increases the conductivity to values more than a hundredfold that of the solvent, but even so, the magnitude of the conductance is comparatively small. The inference to be drawn from this is that the solvent power of these two acids for proteins is not dependent upon an ability on their part to react with the proteins to form protein ions. From the conductivity values of table 1, there can be no question regarding this view about lactic acid. However, to accept the same viewpoint for acetic acid, the increased conductance produced by gelatin, even though small, has to be explained.

That the increased conductivity in these solutions is probably not due to protein salt formation follows from the fact that the conductivity increases

TABLE 1

Specific conductivity of certain proteins in glacial lactic and acetic acids

CASEIN IN LACTIC ACID		EDESTIN IN LACTIC ACID		GELATIN IN LACTIC ACID		GELATIN IN ACETIC ACID	
Concentration	Specific conductivity	Concentration	Specific conductivity	Concentration	Specific conductivity	Concentration	Specific conductivity
g. per liter of solvent	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5
0	5.14	0	5.25	0	7.37	0	0.01 (about)
2.80	5.06	2.85	5.24	4.30	7.48	27.0	1.22
5.65	4.95	5.70	5.23	8.60	7.53	36.0	1.97
8.45	4.93	8.55	5.30	13.00	7.75	45.0	2.75
11.25	4.90	11.40	5.34	17.30	8.03	54.0	3.64
14.05	4.88	14.25	5.46	21.60	8.11	63.0	4.71
16.90	4.87	17.10	5.49	26.00	8.52	72.0	5.79
19.70	4.86	19.95	5.53	30.30	8.82		
22.50	4.96	22.80	5.56	36.10	9.03		
25.30	4.97						
28.15	5.04						

TABLE 2

Conductivity of casein in formic acid

CONCENTRATION	X SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 990$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ	CONCENTRATION	X SPECIFIC CONDUCTIVITY†	EQUIVALENT CONCENTRATION $N = 990$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ
Casein I				Casein II			
g. per liter of solvent	*mhos* × 10^5		*mhos*	*g. per liter of solvent*	*mhos* × 10^5		*mhos*
4.55	17.3	0.0046	37.7	1.90	7.2	0.0019	38.0
9.30	37.6	0.0094	40.0	4.70	17.3	0.0047	36.8
13.90	55.1	0.0140	39.3	9.45	39.9	0.0095	42.0
18.55	73.2	0.0187	39.1	14.15	56.6	0.0143	39.6
23.20	95.8	0.0235	41.7	18.90	74.6	0.0191	39.1
25.10	102.8	0.0254	41.5	23.60	91.6	0.0239	38.3
27.85	110.6	0.0282	39.2	28.30	109.1	0.0286	38.2
32.50	121.1	0.0328	36.7	33.10	126.7	0.0334	38.0
39.10	138.8	0.0395	35.2	37.85	140.4	0.0382	36.8
46.40	169.8	0.0470	36.2	47.20	170.5	0.0477	35.8
55.70	200.0	0.0563	35.5	56.65	198.4	0.0572	34.7

* Specific conductivity of solvent = 14.0 × 10^{-5} mhos has been subtracted from the total.

† Specific conductivity of solvent = 10.15 × 10^{-5} mhos has been subtracted from the total.

much more than proportionally to the gelatin concentration. Doubling the gelatin content produces about a threefold increase in conductance. This increase may well be due to the effect of the moisture added with the gelatin. In qualitative tests it was found that small quantities of water markedly increased the conductance of glacial acetic acid. The gelatin employed had a 10 per cent moisture content.

TABLE 3

Conductivity of edestin in formic acid

CONCENTRATION	κ SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 640$ (DYE TITRATION VALUE)	Λ	EQUIVALENT CONCENTRATION $N = 750$ (HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* $\times 10^5$		*mhos*		*mhos*
4.75	29.7	0.0074	40.1	0.0063	47.2
9.50	55.9	0.0148	37.8	0.0127	44.0
14.25	85.4	0.0223	38.3	0.0190	45.0
19.00	115.3	0.0297	38.9	0.0254	45.4
23.80	144.7	0.0372	38.9	0.0318	45.5
28.50	165.1	0.0445	37.1	0.0380	43.5
33.30	195.7	0.0518	37.8	0.0444	44.0
38.10	216.8	0.0595	36.5	0.0508	42.7

* Specific conductivity of solvent = 10.15×10^{-5} mhos has been subtracted from total.

TABLE 4

Conductivity of gelatin in formic acid

CONCENTRATION	κ SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 950$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* $\times 10^5$		*mhos*
9.0	37.5	0.0095	39.5
18.0	77.0	0.0190	40.5
27.0	116.1	0.0285	40.8
36.0	151.9	0.0379	40.0
45.0	185.4	0.0475	39.0
54.0	217.1	0.0568	38.2

* Specific conductivity of solvent = 10.8×10^{-5} mhos has been subtracted from the total.

Even if it were granted that the conductivity increase is due to protein ionization, a rough calculation shows that the density of charge produced must be very small. Assuming the equivalent conductivity of gelatin acetate would be of the same order as of gelatin formate (table 4), it is calculable from the data of table 1 that the gelatin would have one equivalent of charge for each 75,000 to 100,000 grams. This figure can hardly be as much as one charge per protein molecule. From this evidence another explanation must be sought for the ability of lactic and acetic acids to dissolve proteins than through an interaction to form protein ions. The true explanation of the solvent power remains to be determined.

Conductivity in formic acid

On the other hand, it can hardly be doubted that formic acid reacts with proteins to give ionized protein salts. In tables 2 to 5 are recorded the conductivity values of solutions of casein, edestin, gelatin, and deaminized gelatin in 100 per cent glacial formic acid. These proteins all markedly increase the specific conductivity of the formic acid, the increase being nearly proportional to the amount of protein in solution. The casein measurements were carried out on two separately prepared samples and in different lots of the solvent. The good agreement between the two series is evidence that the conductivity is an intrinsic property of the protein and not of any contamination therein. The magnitude of the conductivity values attained is quite considerable, being nearly of the same order as is found with solutions of the alkali and alkaline earth formates in formic acid. While the ionization reaction is probably no more essential to account for the solvent properties of formic acid than for the other organic acids, still it must be beneficial in this respect and it indicates why formic acid is a so much more powerful solvent than either lactic or acetic acid.

TABLE 5

Conductivity of deaminized gelatin in formic acid

CONCENTRATION	X SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 1705$ (DYE TITRATION VALUE)	Λ	EQUIVALENT CONCENTRATION $N = 1515$ (HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* $\times 10^5$		*mhos*		*mhos*
10.0	25.7	0.0059	43.6	0.0066	39.0
20.0	53.4	0.0117	45.6	0.0132	40.4
30.0	77.1	0.0176	43.8	0.0198	38.9
40.0	90.8	0.0235	38.6	0.0264	34.4
50.0	126.0	0.0294	42.9	0.0331	38.1
60.0	147.4	0.0352	41.9	0.0397	37.2

* Specific conductivity of solvent = 10.8×10^{-6} mhos has been subtracted from the total.

To obtain a more quantitative picture of the electrochemical nature of the protein solutions, it is desirable to evaluate the values for the equivalent conductivity. But to obtain these physical quantities for the proteins in formic acid is a problem offering formidable difficulties because of the uncertainty of the equivalent weights of the proteins.[3]

We were aware of no means by which it would be possible to determine the equivalent weights of proteins in these solutions directly. The extent of the interaction between the proteins and formic acid is unknown, and in aqueous solutions of acid or alkali the equivalent weight of a protein is not a constant but instead varies with the pH, so an estimate is not readily obtained in this way.

The only possible method of approach appears to be through the application of plausible assumptions regarding the equivalent weight, derived from other sources. With such an approach, to obtain what seemed a reasonable estimate of the equivalent weights, recourse was had to the following: From the many studies on the acid combination of proteins in aqueous solution, it has become probable that the maximum combining capacity in this medium is determined by the content of the amino acids, arginine, histidine, and lysine, in a protein. Chapman, Greenberg, and Schmidt (3) have shown that the titration of proteins with acid dyes is in good agreement with this view. Because of the huge excess of formic acid it may be reasoned that the basic groups of the proteins are completely neutralized in formic acid solution. Accordingly, it seems not improbable that the equivalent weight of a protein in formic acid solution may be measured by the value given by the content of arginine, histidine, and lysine or, what usually closely agrees with it, the dye titration figure.

On the basis of this assumption, the equivalent conductivities of casein, edestin, gelatin, and deaminized gelatin were calculated from the content of the hexone bases as determined by Van Slyke (see ref. 3) and, where there was a significant difference, also from the dye titration data of Chapman, Greenberg, and Schmidt. The results of these calculations are incorporated in tables 2 to 5 for each of the proteins respectively under the columns designated by the symbol Λ. The equivalent weight chosen for casein in table 2 is 990, which is the average of the value from the dye titration of 1000 and the hexone base content of 980. The equivalent weight of 950, chosen for gelatin (table 4), also is the mean of the figures from dye titrations and the hexone base content. For the other two proteins separate calculations are given, using values of equivalent weight derived from both of the above sources.

The equivalent conductivity of all four measured proteins has nearly the same calculated values. This correspondence upholds the choice of the equivalent weights, since because of their closely related properties, it may well be expected that the mobility of the proteins in formic acid would be virtually the same. An erroneous basis for the selection of the equivalent weights would be expected to lead to widely varying calculated values of Λ. The close correspondence in equivalent conductivity, it is true, is mainly determined by the high value of the mobility of formate ion in comparison with the mobilities of other ions in formic acid. The work of Schlesinger and coworkers (19, 20) shows that a similar condition prevails among the alkali and alkaline earth formates. The magnitude of the equivalent conductances obtained with the proteins seems plausible when compared with the values for the alkali and alkaline earth formates.

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[3] This is an illustration of the great importance which the equivalent weights have for the solution of electrochemical problems and of how baffling the formulation of the electrochemical state is without these constants.

Most interesting are the results with gelatin and deaminized gelatin. The calculated values of the equivalent conductivities are about the same for each, and both agree well with the figures obtained for casein and edestin even though it is to be remembered that the equivalent weight of the deaminized gelatin has been deliberately altered by the removal of the ϵ-amino group of lysine through interaction with nitrous acid. That the calculations based on this known change should give such harmonizing results is strongly in favor of the reasoning given here.

The results obtained lead to the picture that the proteins in formic acid form ionizable salts rather analogous in electrochemical behavior to the alkali and alkaline earth formates in formic acid. The proteins behave in a manner that might be expected of formic acid salts of rather high valency.

Electrical transference

Since the conductivity curves of the proteins are not satisfactory for the purpose of evaluating the limiting equivalent conductivities at infinite dilutions, a number of electrical transference experiments were carried out to get at this data. The Hittorf method was employed in the first instance. The cell, with some slight modifications, was the type introduced by Landsteiner and Pauli (15). Five electrode portions were obtainable for analysis, but experience soon showed that only in the outermost anode and cathode portions was there produced any concentration change. The electrodes were of platinum wire and no correction was applied for the hydrogen evolved at the cathode and carbon dioxide at the anode, which have been shown by Schlesinger and Bunting (17) to be the main products of the electrode reactions. The current passing through the cell during the course of an experiment was measured with an iodine coulometer. A motor generator developing a D. C. current at a voltage of 250 supplied the current for electrolysis.

Naturally, the change in formate ion was not measurable, so only the change in protein content could be followed. This was determined by Kjeldahl analysis of the nitrogen content. The results obtained on each of the proteins are given in table 7. As the table shows, very closely agreeing figures were obtained from both cathode and anode portions in repeated experiments. From the transference numbers the Λ^0 values of the proteins shown in table 6 were calculated, using the value of 51.6 for the equivalent conductivity of formate ion as given by Schlesinger and Bunting (19). Compared to the figures in aqueous solution, the protein-

TABLE 6

Electrical transference of proteins in formic acid

Temperature, 25°C.

a. Casein

EXPERIMENT NO.	CASEIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	CASEIN CHANGE IN COMPARTMENT		T^+_{casein}
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*	
1	30.0	0.455	Anode	17.5	0.443	−42.4	−0.043	0.095
		0.455	Cathode	17.0	0.430	+41.6	+0.042	0.092
2	30.0	1.065	Anode	19.6	0.995	−95.5	−0.097	0.090
		1.065	Cathode	17.5	1.025	+97.5	+0.099	0.093
Average								0.093
Λ^{0+}_{casein}								5.5

b. Edestin

EXPERIMENT NO.	EDESTIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	EDESTIN CHANGE IN COMPARTMENT	EDESTIN CHANGE $N = 640$	$T^+_{edestin}$	EDESTIN CHANGE $N = 750$	$T^+_{edestin}$
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*		*milliequivalents*	
3	27.0	1.360	Anode	20.1	1.68	−121	−0.189	0.14	−0.161	0.12
4	28.5	0.775	Anode	18.8	1.00	−76	−0.1175	0.15	−0.1015	0.135
		0.775	Cathode	18.6	0.99	+75	+0.117	0.15	+0.1000	0.13
Average								0.15		0.13
$\Lambda^{0+}_{edestin}$								9.0		7.7

c. Gelatin

EXPERIMENT NO.	GELATIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	GELATIN CHANGE IN COMPARTMENT $N = 950$		$T^+_{gelatin}$
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*	
5	30	1.27	Anode	17.8	0.554	−153	−0.160	0.125
	30	1.27	Cathode	16.4	0.562	+144	+0.150	0.12
Average								0.12
$\Lambda^{0+}_{gelatin}$								7.2

TABLE 6—*Concluded*

d. Deaminized gelatin

EXPERIMENT NO.	DEAMINIZED GELATIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	DEAMINIZED GELATIN CHANGE IN COMPARTMENT	DEAMINIZED GELATIN CHANGE $N = 1705$	$T^+_{\text{deaminized gelatin}}$	DEAMINIZED GELATIN CHANGE $N = 1515$	$T^+_{\text{deaminized gelatin}}$
	g per liter	*milli-equivalents*		*ml.*	*milli-equivalents*	*mg.*	*milli-equivalents*		*milli-equivalents*	
6	30	1.27	Anode	16.8	0.444	−121	−0.071	0.056	0.08	0.063
	30	1.27	Cathode	18.8	0.419	+127	+0.0745	0.059	0.084	0.066
Average								0.058		0.064
$A^{0+}_{\text{deaminized gelatin}}$										3.5

TABLE 7

Electromotive force cells and transference of sodium formate in formic acid

Temperature = 25°C.; reference concentration = 0.147 molal sodium formate

CONCENTRATION OF SODIUM FORMATE		E (MEASURED)	T_{Na^+}
per cent	*moles per liter of solvent*	*volts*	
0.10	0.0147	0.0286	0.241
0.15	0.0220	0.0236	0.241
0.20	0.0294	0.0197	0.238
0.25	0.0367	0.0164	0.232
0.30	0.0441	0.0142	0.230
0.35	0.0514	0.0123	0.236
0.40	0.0588	0.0110	0.236
0.45	0.0662	0.0090	0.220
1.00	0.1470	0.0000	
Average			0.236

ion mobility in formic acid is astonishingly low, but it is quite concordant with the figures for the mobility of the cations of the alkali and alkaline earth elements in formic acid obtained by Schlesinger and associates.

It was also attempted to determine the transference numbers of formic acid solutions through the use of electromotive force cells with transference. Since Hall and Conant (6) have shown that certain oxidation–reduction couples can be used to measure the hydrogen-ion activity in such nonaqueous solvents as acetic acid, it seemed not unlikely that the quinhydrone electrode could be used for this purpose in formic acid. Tests showed that this electrode worked well in the presence of the alkali formates, but unfortunately, not with solutions of proteins in formic acid. This may be due to an interaction between quinone and the proteins, similar to the reaction which occurs in the quinone leather tanning process (see ref. 23).

Although no valid results were obtained with the proteins, the data obtained with sodium formate will be presented, since the method offers an independent means of obtaining such information that has hitherto, as far as we are aware, not been employed for non-aqueous solutions.

The cell set-up for the measurements is given by the equation,

$$\underset{E_1}{\mathrm{Pt}\,|}\ \text{Quinhydrone, }[\mathrm{NaOOCH}]_1 \underset{E_3}{|} [\mathrm{NaOOCH}]_2\text{, Quinhydrone}\ \underset{E_2}{|\,\mathrm{Pt}} \qquad (1)$$

The electromotive force of this cell (5), as can be readily shown, is given by equation 2 below, provided the mass law relationship, $[\mathrm{H}^+]\,[\mathrm{HCOO}^-] = k$ holds in formic acid.

$$E = E_2 - E_1 + E_3 = 2T_c \frac{RT}{F} \ln \frac{[\mathrm{NaOOCH}]_2}{[\mathrm{NaOOCH}]_1} \qquad (2)$$

where T_c is the cation transference number. At 25°C., using numerical values of the constants, the equation becomes

$$E = 0.118\ T_c \log \frac{[\mathrm{NaOOCH}]_2}{[\mathrm{NaOOCH}]_1} \qquad (3)$$

In carrying out the measurements, the liquid junction in the cell was established by plugging a stopcock which connected the two arms of the cell with cotton wool so that only a slow diffusion of liquid obtained. With this arrangement it was found that after a few minutes to allow for the attainment of diffusion equilibrium, a very steady and reproducible electromotive force was established. Since quinhydrone is quite soluble in formic acid, it was introduced just before the start of an experiment in amounts required to make the concentration in each arm of the cell the same.

The results obtained with the sodium formate solutions are recorded in table 7. With the concentrations of sodium formate employed of between 0.0147 and 0.066 molal, the transference numbers found for sodium ion are reasonably constant. The average value of 0.236 for the sodium ion transference number, while not identical with the value of 0.22 obtained by Schlesinger and Bunting by the Hittorf method, is perhaps in as good agreement as might reasonably be expected, since no great degree of refinement marks the results by either procedure.

SUMMARY

1. Measurements of the conductivity of solutions of proteins in the glacial carbon acids, lactic, acetic, and formic have been carried out. In lactic and acetic acids this is increased but little. On the other hand, a marked

conductivity increase is produced in anhydrous formic acid, so that the solutions become nearly as good conductors as are solutions of the alkali and alkaline earth formates in formic acid.

2. On the basis of certain plausible appearing assumptions the equivalent conductivity of the proteins casein, edestin, gelatin, and deaminized gelatin in formic acid has been calculated.

3. Transference numbers of the protein formates have been determined by the Hittorf method. The results of the conductivity and transference measurements lead to the picture that the proteins in formic acid form ionizable salts having electrochemical properties which would be expected of formic acid salts of rather high valency.

4. Measurements of the transference numbers of sodium formate in formic acid have been carried out by means of an electromotive force cell with transference.

5. The solvent action of the three glacial acids used in this work for proteins does not appear to be particularly dependent upon their ability to form electrically charged protein ions.

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THE ADSORPTION OF THE VAPORS OF CERTAIN KETONES AND ESTERS BY ACTIVATED CHARCOAL[1]

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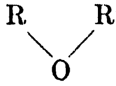
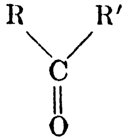
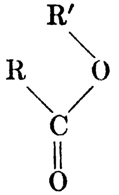
Previous investigations (4) have dealt with the adsorption of vapors of various types by activated charcoal. These have been studied with special reference to the influence of the position and the nature of substituent groups in the vapor molecules upon adsorption magnitudes. In this paper we present the results obtained in the study of the adsorption of certain ketone and ester vapors by charcoal. If these are considered in conjunction with the vapors of ethers previously studied (6), we have three types of oxygen compounds to consider, namely,


Ether


Ketone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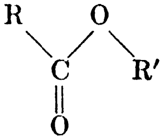
II

Ester

The mobility of the molecules on an adsorbing surface supports the view that adsorption is a phenomenon due to physical attraction. These forces may be simply van der Waals forces or they may be of an electrical nature, depending upon the dipole nature of the vapor molecules. Under the influence of the powerful surface forces the molecular dipoles will be definitely oriented and attracted by the surface atoms.

According to Eucken and Meyer (2), the dipole moment of a molecule is the vector sum of the partial moments of the individual linkages of the atoms in the molecule. They have calculated the moments of the following typical linkages:

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[1] A brief extract of a dissertation presented by Arthur C. Hanson to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Linkages......	H—C	H—O	C═O	C—C	C—OH	$C{-}C^{O}_{H}$
$\mu \times 10^{18}$ E.S.U.	0.4	1.6	2.3	0.7	1.6	1.0

They have added vectorially the four moments in the ester molecule, R·COO·R′, and they have found the moments for formulas I and II to be 3.4×10^{-18} and 1.1×10^{-18} E.S.U., respectively. Since the moment of the H—(C) should be the same as that of CH_3—(C), or of $CH_3 \cdot [CH_2]_n$—(C), the moments should be independent of the nature of the radical R, provided it consists of hydrogen atoms, or of alkyl groups only.

Except as modified by the remaining linkage moments, the C═O moment is the one specifically active in the adsorption of ketone vapors. Its value should be affected considerably by the presence and the manner of rotation of the R—O— dipoles in the ester molecule. The moments of the fatty acids are approximately 1.4×10^{-18} and of most esters about 1.8×10^{-18} E.S.U.

According to Debye (1), the two possible angles between the two H—O linkages of the water molecule are 64° and 110°, respectively; the corresponding moments calculated for these angular dimensions are 1.34×10^{-18} and 4.34×10^{-18} E.S.U. The actual observed moment lies between these at about 1.8×10^{-18}. It is conceivable that by repulsion between substituted groups the moments of the ether molecules, R_2O, should be different from that of their prototype, H_2O, and yet be only slightly affected by the size of the alkyl groups.

With these considerations in mind, it should be quite evident that whether we consider the ethers, the ketones, or the esters separately as a class, the magnitude of the adsorption due to the dipole moment will be but slightly modified by the complexity of the molecules of the given type.

While the moments of the molecules are undoubtedly effective in adsorption, the relative amounts adsorbed for the different vapors of any one class will depend to a large degree upon certain other physical properties. Among these are the cross-sectional area of the molecules, the ease of condensation, or the boiling points of the pure liquids, and the van der Waals constants "*a*."

If it is assumed that the vector moment is the same in the ether and ketone molecules oriented at the surface, it is evident that the surface covering power of dimethyl ether should be practically the same as that of dimethyl ketone. The surface covering power of either one must be less than that of the corresponding diethyl compound. With either type the covering power must increase with increase in the complexity of the substituted alkyl groups.

In so far as the previous work has shown, the adsorption of any vapor at low pressures is greater the higher the boiling point of the pure liquid.

TABLE 1

The adsorption of acetone vapor by charcoal at various temperatures

At 0°C.												
p......	0.00	0.00	0.20	0.55	1 24	3.52	5.16	12.41	28.19	33 69	44.87	50 58
x/m...	12 23	25.40	60 88	75.45	85.48	94.20	97 94	102 80	109.06	110.64	114.59	116 90
p......	61.00	64 58	70.08									
x/m...	120.87	122.74	131.67									
At 40°C.												
p........	0.10	0.35	0 55	0 69	0 79	1.55	2.28	3 52	4 46	9.03	12.02	
x/m.. ..	6 33	20 17	25 48	31.10	34 74	45 57	60 65	67 59	72.28	83.13	86 93	
p...... .	18 02	24 07	27 00	37 72	52 12	78 42	89.89	154 47	243 51	288.68		
x/m .	91.83	95 28	96 10	99 34	101 45	104 36	105 49	109.62	114 48	116 51		
p.... .	337.92	388 26	420 91	421 50	412 17							
x/m	119 29	121 26	128 10	129 74	122 93							
At 56.3°C.												
p............	0 30	0.89	1 89	4 25	6 70	12 57	16 88	17 22	24.80	37 67	45 54	
x/m..........	10 01	19 12	31.05	49 98	58 97	70 50	75 06	75 20	80.57	86.30	88.65	
p..	56 14	80.38	112 92	158.29	164.64	228.62	281 32	421 51	437.04			
x/m..........	91 12	93 93	96 64	99.37	99.81	102.21	103 84	108 90	109.07			
At 99.48°C.												
p.....	1.09	1.84	4.17	8.79	15.29	17.52	32.61	39.21	56.58	58.72	75.60	86.82
x/m..	5.88	7.76	13.77	22.90	31 36	33.68	44 74	47.57	53.85	56.05	62.80	66.15
p	88.00	88.45	112.77	137.49	169.01	183 60	204.10	233 59	288.09	358 12	422.64	
x/m..	66.56	66.56	71.38	75.06	77.94	79 21	80.73	82.35	84.49	86.95	89 58	
At 138.27°C.												
p........	2 00	7.69	10.32	35.24	66.11	112 72	161.56	248 53	297.72	315 48	405 97	419.95
x/m.....	4.38	10.68	13.21	25.63	36 32	46.48	52.98	60 66	63 38	64 24	68.93	71.50
At 183.10°C.												
p........	14.14	38.09	76.08	125.16	183.66	248.20	308.35	370 85	415.00	420.93		
x/m......	4.46	9.29	15.48	22.11	28.09	32.57	36.50	40.20	42.80	46.47		

Here, also, the cross-sectional area exerts a specific influence. The first molecules admitted to the surface are adsorbed without definite arrangement with respect to the surface atoms. Before the surface can become completely covered at saturation there must be a movement of the molecules along the surface, or a rotation about their points of attachment. For this reason more time is required for the attainment of adsorption equilibrium (5), and this influence will be greater, the greater the cross-section and the complexity of the molecules.

TABLE 2

The adsorption of methyl ethyl ketone vapor by charcoal at various temperatures

At 0°C.												
p	0.00	0.00	0.25	0.74	0.86	2.45	3.92	6.50	8.28	12.25	17.99	21.21
x/m	43.47	44.22	60.98	83.50	83.72	89.39	91.91	94.26	96.17	98.40	102.79	105.85
p	24.93	25.27										
x/m	108.43	112 91										
At 50°C.												
p	0.79	3.12	3.72	5.95	8.72	16.60	30.23	65.36	160.10	220 30	290.10	295.92
x/m	27.82	53.73	57.60	64.04	67.72	76.03	80.15	84.56	90.48	92.50	94 05	96.08
At 79.5°C.												
p	0.15	0.60	1.85	5.75	8.42	9.32	19.28	29.68	52.77	105.47	172.40	237.20
x/m	9.98	19.66	35.34	50.04	56.54	57.00	65.27	69.44	72.95	76.80	80 00	81 88
p	279.27	297.43										
x/m	83.33	85.57										
At 139.15°C.												
p	4 71	13.33	24.25	43.31	62.69	63.23	91.97	98.11	98.56	125.56	165 56	184.94
x/m	16 86	27.60	36.45	45.63	51.24	51.31	55.97	56.96	57.36	59.95	62.94	64.11
p	274.34	298.22										
x/m	68.45	76.65										
At 181.2°C.												
p	6 84	20.05	39.84	82.41	139.35	217.70	275.92	295.20				
x/m	9.59	21.03	30.33	37.54	45.19	51.49	54.41	55.03				

The apparatus, charcoal, and the technique involved are the same as that employed in all of the previous work. The ketones and esters were Eastman's products of highest purity. They were further purified according to approved standard methods and several times fractionally distilled, using the apparatus designed by Loveless (3). Only the final middle fractions distilling over within a range of 0.01° to 0.10°C. at the correct boiling point were used.

The complete experimental data, including all duplicate series, are collected in the following tables. In these p is the equilibrium pressure in millimeters and x/m is the number of cubic centimeters (N.T.P.) of vapor adsorbed by 1 g. of charcoal.

TABLE 3

The adsorption of diethyl acetone vapor by charcoal at various temperatures

At 0°C.

p	0.00	0.30	0.64	1.30	1.65	5.35	7.91	9.61	9.68
x/m	40.18	73.43	76.40	81.66	83.28	88.39	91.49	97.39	98.85

At 40°C.

p	0.00	0.10	0.35	0.70	2.61	4.43	11.68	16.93	21.39	28.13	30.08
x/m	24.09	34.39	50.18	55.09	65.31	68.68	74.22	76.19	77.31	78.83	79.23
p	31.87	53.02	56.14	63.74	68.45	70.49	95.20	120.15	120.68		
x/m	79.60	83.61	84.32	85.62	86.35	87.35	90.85	95.30	97.72		

At 99.4°C.

p	0.35	0.84	1.78	1.95	4.02	5.43	9.81	10.79	14.42	23.06
x/m	28.00	35.19	42.34	43.16	49.57	52.45	57.65	58.36	60.29	62.93
p	24.89	36.22	69.28	93.90	115.46	119.77				
x/m	63.28	65.11	67.87	69.25	70.15	72.62				

At 139.09°C.

p	0.40	1.55	2.79	5.85	5.92	6.95	8.68	11.01	14.42	16.67	19.00
x/m	10.34	21.19	28.68	37.25	39.66	39.66	42.57	45.62	48.57	49.66	51.38
p	21.82	34.04	39.15	59.02	90.00	117.94	118.68				
x/m	52.49	55.02	55.48	57.36	60.30	62.26	64.37				

At 182.4°C.

p	0.80	1.88	4.08	5.49	9.06	10.40	15.61	22.30	26.22	39.62	50.64
x/m	9.73	15.43	21.58	24.58	29.87	31.01	34.95	38.03	39.06	43.60	45.64
p	77.31	102.03	114.08	119.70							
x/m	49.17	51.38	53.09	55.40							

For want of a better method we have made use of the Langmuir equation for adsorption on a plane surface and we have plotted the values of $p/(x/m)$ against the corresponding pressures, p. The Langmuir isotherms thus obtained for low pressures at various temperatures are shown in figures 1 and 2; those for the boiling points at higher pressures are shown in figure 3. Within the range indicated by the experimental points, the Langmuir equation satisfactorily expresses the adsorption relations. At still higher pressures, however, the experimental points deviate widely from the straight line plot.

The influence of the structure and molecular complexity of the ether, ketone, and ester vapor molecules is perhaps best shown by the natural boiling point isotherms, $x/m = ap^n$. At the boiling point the tendency of the vapors to condense is practically eliminated. The only forces prevailing are those between the adsorbent and the vapor molecules and the van der Waals forces between the molecules in the vapor phase.

TABLE 4

The adsorption of ethyl formate vapor by charcoal at various temperatures

At 0°C.												
p	0.10	0.20	0.60	2.98	7.25	12.91	21.94	30.58	40.95	50.33	59.47	69.94
x/m	37.79	60.69	82.01	92.61	96.96	99.47	102.39	104.74	107.65	110.27	112.53	114.55
p	73.41											
x/m	117.88											
At 40°C.												
p	0.05	0.25	1.25	3.57	6.66	7.89	13.10	17.62	29.63	44.77	89.89	
x/m	16.89	30.56	44.06	59.54	71.13	74.50	79.47	81.27	85.79	88.86	93.14	
p	129.01	172.24	238.75	300.01	322.99	377.64	397.49	448.37	448.72			
x/m	94.90	96.83	99.41	102.18	103.12	105.68	106.24	108.64	110.85			
At 54.4°C.												
p	0.30	0.50	1.09	1.24	2.43	3.91	4.21	7.53	10.40	12.82	17.08	
x/m	9.50	13.52	22.90	24.01	35.30	44.28	46.42	56.76	61.63	65.52	69.75	
p	25.05	33.52	47.53	63.08	80.80	88.08	176.56	224.94	243.25	370.85		
x/m	74.74	78.55	81.51	84.75	86.27	87.55	91.13	92.62	93.68	96.40		
p	371.84	464.97	580.33									
x/m	96.82	98.21	100.55									

The natural boiling point isotherms, figure 4, show definite characteristic regularities. Ethyl formate is less adsorbed at all pressures than is methyl acetate. At pressures below 0.2 mm. the order of increasing adsorption for the acetate vapors is: methyl < ethyl < propyl. At higher pressures the order is exactly reversed. Methyl propionate is less adsorbed than are ethyl and propyl acetates at pressures below 0.8 mm.;

it is more highly adsorbed than methyl acetate below 1.5 mm. The higher boiling *n*-propyl acetate is the most highly adsorbed of all the esters at low and least at high pressures. The order of adsorption of all the esters at pressures below 0.8 mm. is

TABLE 5

The adsorption of methyl acetate vapor by charcoal at various temperatures

At 0°C.

p	0.10	0.20	0.35	0.40	2.38	6 16	16 08	16.63	33.31	48.50	55.40
x/m	38.94	59.99	71.10	78.71	92.66	97.61	102 94	103.05	108.75	114.11	115.95
p	59.56	63.04	63.34								
x/m	116.65	123.81	123.12								

At 40°C.

p	0.20	0.30	1.29	5.91	7.15	23.08	26.91	54.26	78.43	125.84
x/m	20.85	35.51	54.07	75.42	77.59	87.98	88.64	92.91	95.25	97.88
p	190.51	234.80	309.78	332.67	360.69	391.44	394.94			
x/m	101.62	103.49	108.22	109.58	110.26	112.65	121.08			

At 57.10°C.

p	0.10	0.94	3.67	7.13	17.39	24.91	40.96	71.22	109.26	258.99
x/m	6.52	35.96	55.88	65.24	76.49	81.41	85.82	88.79	91.29	96.59
p	351.66	428.08	447.96	573.13	754.03					
x/m	99.08	101.21	101.89	105.66	110.91					

At 99.71°C.

p	1.04	3.20	12.75	16.03	28.69	43.18	60.46	76.14	129.40	184.25
x/m	13.12	22.70	41 50	43.75	52.66	58.91	63.74	66 81	72.20	76.55
p	244.16	310 98	380.27	402.26						
x/m	79.01	81.56	82.98	85.52						

At 139.46°C.

p	6.16	10.92	15.88	38.07	68.35	135.91	177.65	221.47	261.34	327.06	376.55	405.43
x/m	16.14	21.84	26.06	38.11	45.76	56.26	60.41	64.10	65.93	68.97	70.07	72.50

Ester	*n*-AcOPr	>	AcOEt	>	PrOMe	>	AcOMe	>	FOEt
$a \times 10^5$(atms.)[2]	5144		4076		4027		3137		3128
$\mu \times 10^{18}$ (E.S.U.)	1.78		1.81		1.69		1.76		1.92

---

[2] The van der Waals constants, a, were taken from or calculated by formulas given in Landolt-Börnstein, Physikalische-Chemische Tabellen, 5th edition, Vol. I, p. 253. Springer, Berlin (1923).

TABLE 6

The adsorption of ethyl acetate vapor by charcoal at various temperatures

At 0°C.

p........	0.00	0.05	0.10	0.30	0.40	2.63	2.98	6.30	9.58	10.82	15.88
x/m.....	17.06	34.28	40.13	66.88	75.21	81.59	82.36	85.08	87.69	88.60	91.97
p........	17.37	20.50	24.47								
x/m.....	92.85	94.09	99.01								

At 40°C.

p...........	0.00	0.05	0.10	0.50	0.98	1.24	1.54	8.49	14.74	15.19	32.41
x/m.	6.90	20.39	21.68	47.54	50.86	63.69	64.57	71.92	75.26	75.55	78.50
p...........	43.09	49.64	50.13	83.39	104.34	111.58	117.14	135.36	141.81		
x/m.........	79.26	79.99	80.33	83.12	84.60	85.62	85.37	87.83	87.88		
p...........	143.29	166.58	183.66								
x/m	88.36	89.91	91.29								

At 76.06°C.

p........	0.05	0.20	0.25	0.35	0.89	3.18	4.67	9.78	18.47	48.15
x/m. . .	7.93	18.25	21.85	29.46	38.56	52.32	55.63	61.39	66.03	70.30
p........	50.48	100.37	115.06	150.30	180.88	184.95				
x/m.	70.54	73.49	74.15	75.21	76.50	77.48				

At 99.48°C.

p........	0.40	1.54	3.97	8.34	20.95	33.01	41.40	67.21	115.80	132.08
x/m	19.24	31.02	40.41	47.49	55.35	58.67	60.28	63.27	66.03	66.64
p........	153.68	174.03	186.64							
x/m	67.27	67.89	69.24							

At 139.48°C.

p........	0.30	2.98	6.16	13.01	22.24	40.75	48.25	48.60	58.22	87.51
x/m......	13.55	22.61	28.15	34.51	40.83	46.25	48.33	48.76	50.20	53.23
p........	122.90	142.86	167.33	178.59	189.66					
x/m......	55.56	57.07	58.08	58.37	61.57					

At 180.53°C.

p........	1.49	6.01	16.13	37.92	66.51	85.23	141.02	170.01	191.65
x/m.....	9.61	18.34	27.05	36.00	41.78	44.41	49.15	50.68	53.24

This is exactly the order of decreasing boiling points of the liquids; it is also the same order as that of the van der Waals constants.

The order of adsorption at higher pressures is

Ester...........	AcOMe >	FOEt >	AcOEt >	PrOMe >	AcOPr
$a \times 10^5$ (atms.)..	3137	3128	4076	4027	5144

With slight variations due to cross-sectional influences the order here is the reverse of the order of increasing values of the van der Waals a.

TABLE 7

The adsorption of n-propyl acetate vapor by charcoal at various temperatures

At 0°C.

p........	0 00	0 00	1 09	3 77	6.54	7.83
x/m.... .	24 85	52 27	68 52	73 23	76 48	79 98

At 40°C.

p......	0 00	0 00	0 20	0 30	0 50	1 04	2 03	5 26	10 67	17.27
x/m. ..	19.72	26.13	37 94	52 34	54 63	58.17	59 86	63 33	65 23	66 70
p........	22 63	28 09	34 50	38 77	44 52	55 19	58 27	67 60	69 09	71 08
x/m	67 88	68 86	69.72	70 79	71.21	73.25	73.72	74 74	75 17	76.95

At 99.54°C.

p........	0 05	0 64	1 88	5 55	11.45	25.96	55 20	75.32	94 00	115.85	116 54
x/m....	16.00	29 87	41 43	47.96	51 50	54 83	57 38	58.35	59.29	60 51	62 00

At 139.53°C.

p........	0.25	0 74	2 53	4 66	11.50	35 78	61 84	79 78	100 69	116 54
x/m......	11.02	20 08	28 94	33.52	40 62	47 12	49 82	50.88	51 98	52 96

At 181.54°C.

p........	0.50	1.19	3.22	7.68	10.36	15.36	28.24	47.12	68.98	101.38	117.93
x/m.....	5.69	11.13	16.92	23 20	25 11	28 38	33 28	36.71	39 32	41 20	42.99

Similar relations also were found to exist for the adsorption of ketone and ether vapors. The order of adsorption at low pressures is

Ketones......................	Et_2CO >	EtCOMe >	Me_2CO
$a \times 10^5$ (atms.)			
$\mu \times 10^{18}$ E.S.U.......................		2.74	2.74
Ethers............................	Pr_2O >	Et_2O >	Me_2O
$a \times 10^5$.........................		3464	1609
$\mu \times 10^{18}$.........................		1.14	1.29

TABLE 8

The adsorption of methyl propionate vapor by charcoal at various temperatures

At 0°C.

p	0.00	0.05	0.10	0.15	0.25	0.70	0.75	2.98	7.89	9.78	14.00
x/m	14.94	29.99	55.85	64.05	67.87	76.68	77.77	82.23	86.43	87.59	90.26
p	17.72	18.81	21.94	22.14							
x/m	92.79	93.26	95.74	98.51							

At 40°C.

p	0.05	0.10	0.20	0.84	3.90	7.15	26.01	37.28	54.55	74.65	98.08
x/m	16.41	33.31	48.30	61.16	70.02	73.33	78.21	79.63	81.47	83.32	85.63
p	127.72	156.21	168.91								
x/m	88.25	90.63	93.18								

At 79.85°C.

p	0.15	0.45	1.74	3.03	7.00	8.84	11.17	18.96	33.21	45.77	60.26
x/m	11.20	24.85	43.87	49.78	57.25	59.10	60.90	64.30	67.52	68.92	69.99
p	93.47	108.90	123.80	153.13	168.22						
x/m	71.82	72.63	73.09	74.04	76.52						

At 99.88°C.

p	0.25	0.35	1.04	2.98	7.55	12.41	24.92	30.78	48.50	67.36	85.13
x/m	12.14	20.61	27.10	38.68	47.98	52.48	58.30	60.22	63.16	65.06	66.60
p	116.90	152.29	168.87								
x/m	68.03	69.11	70.41								

At 138.73°C.

p	0.25	0.75	2.13	4.27	6.35	12.56	17.77	25.07	31.22	37.03	48.25
x/m	8.25	12.30	18.54	24.51	27.87	34.97	38.16	41.96	44.07	46.00	48.31
p	53.06	87.16	100.22	103.10	146.53	147.42	174.87				
x/m	49.30	53.46	54.69	54.98	57.54	58.22	59.48				

TABLE 9

Heats of adsorption calculated from the isosteres

VAPOR	ΔH	VAPOR	ΔH
	cal.		*cal.*
Acetone	−10690	Methyl acetate	−11520
Methyl ethyl ketone	−11224	Ethyl acetate	−11960
Diethyl ketone	−11020	*n*-Propyl acetate	−13200
Ethyl formate	−13140	Methyl propionate	−14030

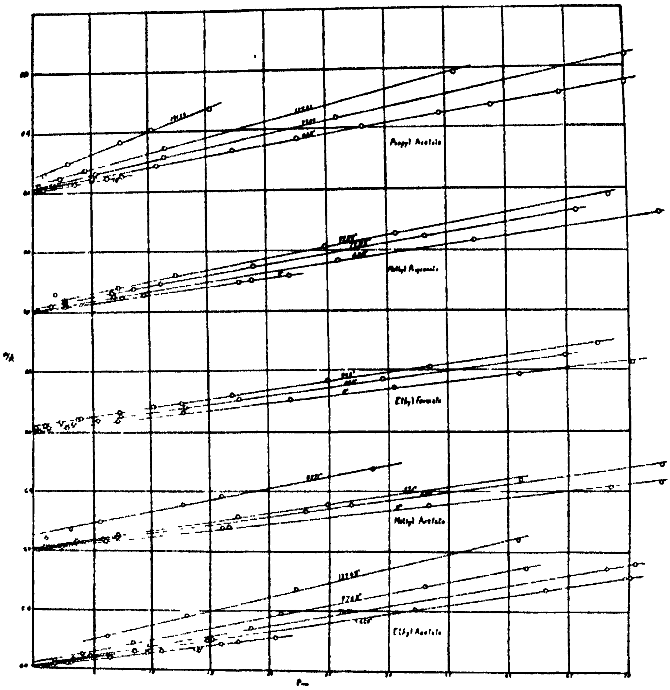

FIG. 1. LANGMUIR ISOTHERMS FOR VARIOUS ESTERS AT DIFFERENT TEMPERATURES

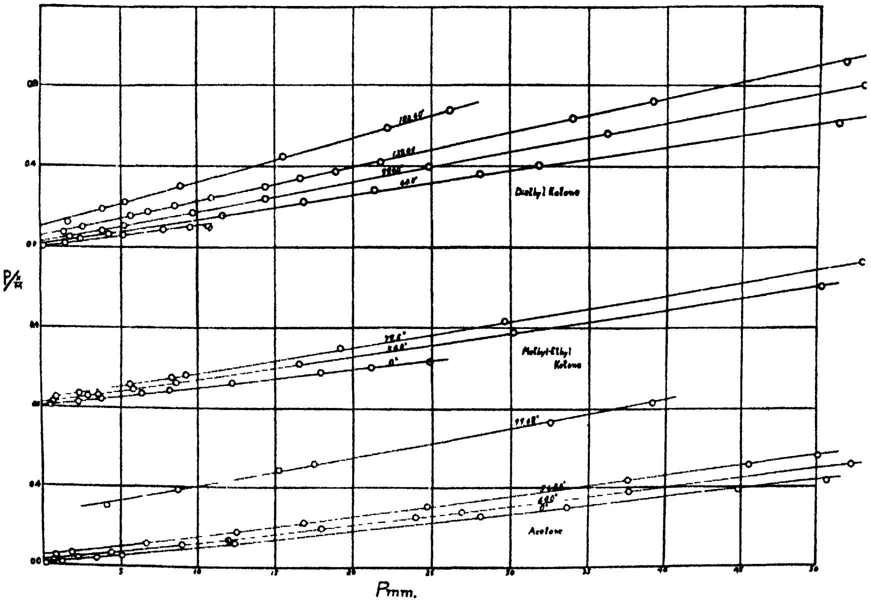

FIG. 2. LANGMUIR ISOTHERMS FOR CERTAIN KETONES AT DIFFERENT TEMPERATURES

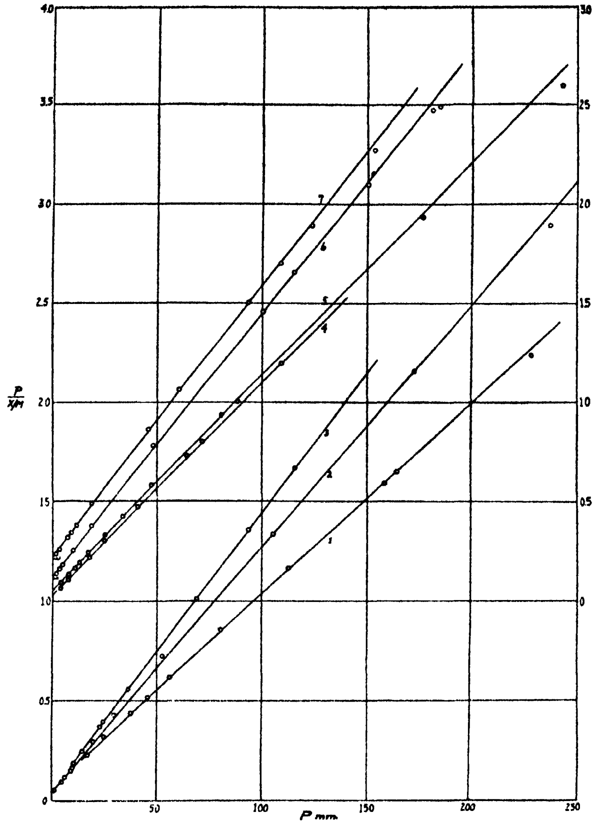

Fig. 3. Langmuir Boiling Point Isotherms

1, Acetone; 2, methyl ethyl ketone; 3, diethyl ketone; 4, methyl acetate; 5, ethyl formate; 6, ethyl acetate; 7, methyl propionate.

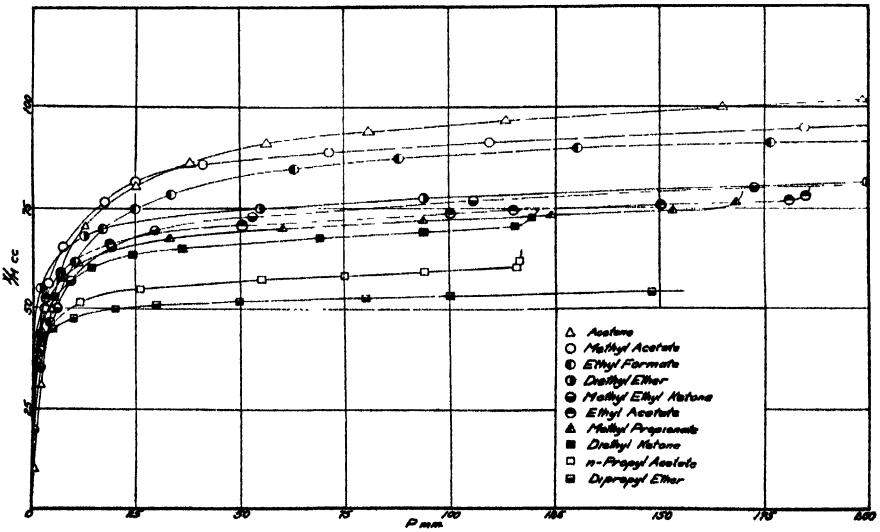

Fig. 4. Natural Isotherms at the Boiling Points

For both the ketones and the ethers the order is again reversed at high pressures. The values of a for the ketones are not available, but they should increase with increase in molecular complexity.

The relations obtained from the study of the natural boiling point isotherms appear to permit two definite conclusions: first, for all vapors of any one class the magnitude of the adsorption is directly dependent upon the van der Waals constant a; second, the magnitude of adsorption is independent of the dipole strength of the vapor molecules, or their influence is masked by other factors.

The isosteres were plotted for the ketone and ester vapors. With the exception of the lowest concentration, the experimental points fall exceedingly well upon straight parallel lines. The heats of adsorption calculated from the slopes of the isosteres are given in table 9.

SUMMARY

The adsorption of certain ketone and ester vapors by activated charcoal has been measured at several temperatures between 0°C. and 182°C.

The Langmuir equation for adsorption on plane surfaces applies for pressures up to approximately 200 mm.

For any series the amount of vapor adsorbed at low pressures is always greatest for the vapor having the highest boiling point; it is less for the simpler low-boiling liquids. At higher pressures the order of adsorption is reversed. Adsorption increases with increase in the value of the van der Waals a, and it appears to be independent of the dipole strength of the vapor molecules.

The heats of adsorption have been calculated from the slopes of the isosteres.

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THE SURFACE BEHAVIOR OF ZEOLITES

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The authors wished to study the surface behavior of zeolites during dehydration by the method previously applied to aged hydrous alumina (2). Accordingly the water content of samples of scolecite and analcite of different average particle sizes was determined under the same conditions. The large particle samples (3×10^3 cm.^{2} apparent surface per gram) and small particle samples (5×10^3 cm.^{2} apparent surface per gram) were kept in weighing bottles in a desiccator at various temperatures and vapor pressures. A few of the many results obtained are given in table 1. As far as the authors could tell these were all equilibrium values, with the exception of sample g, since the water content–time curve had become level.

These results become of special interest when applied to the equation derived earlier (1)

$$c = (w_l w_s' - w_s w_l')/(w_l + w_s' - w_s - w_l')$$

w_l and w_s represent water percentages contained by a pair of zeolite samples (large and small particles) at a given temperature and vapor pressure. w_l' and w_s' represent the percentages of water in the same two samples under different conditions. c will then be the calculated percentage of water in the zeolite when no water adsorption has taken place. Several values for c are given in table 2.

Several interesting conclusions can be drawn from these results. The c values for scolecite are remarkable for their constancy. This fact, coupled with the data in table 1, leads to the conclusion that the water variation of this zeolite was due to a change in surface adsorbed water. The water content within the scolecite lattice did not change appreciably under the conditions of the experiment.

The c values for analcite are also essentially constant. From the data in table 1 the change in water content at the higher vapor pressures was essentially due to a change in positively adsorbed surface water. But at the lower vapor pressure the water content of the small particle analcite sample is lower than that of the large particle sample. This fact, together with the calculated c values, clearly indicates that a surface dehydration took place. Water was lost from the surface portions of the zeolite lattice, forming a zone of skeleton lattice at the surface of the particles. As far as present experiments could show, this was an equilibrium condition.

This case of surface dehydration is an example, on a larger scale, of what the authors believe happens during the dehydration of hydrates and related compounds. It seems likely that with such compounds a condition of surface dehydration may be a stable one, in which true equilibrium can be reached. This conception is discussed more completely in an earlier paper (2).

TABLE 1

Water content of zeolites under various conditions

ZEOLITE	PAIR	WATER PERCENTAGE		SUBSTANCE IN DESICCATOR	TEMPERATURE °C.
		Large particle	Small particle		
Scolecite	a	16.09	16.34	$CuSO_4 \cdot 5H_2O$	23
Scolecite	b	16.15	16.44	$Na_2HPO_4 \cdot 12H_2O$	24
Scolecite	c	15.78	15.90	BaO	50
Scolecite	d	15.56	15.58	BaO	126
Analcite	e	9.388	9.402	$CuSO_4 \cdot 5H_2O$	24
Analcite	f	9.491	9.512	$Na_2HPO_4 \cdot 12H_2O$	23
Analcite	g	9.214	9.143	P_2O_5, vacuum	22
Analcite	h	9.135	9.056	P_2O_5, vacuum	21

TABLE 2

Calculated water content for zeolites when no adsorption takes place

ZEOLITE	PAIRS	c	ZEOLITE	PAIRS	c
Scolecite	a, c	15.54	Analcite	e, h	9.35
Scolecite	b, c	15.52	Analcite	f, h	9.42
Scolecite	a, d	15.48	Analcite	e, g	9.36
Scolecite	b, d	15.48	Analcite	f, g	9.43

These results throw a somewhat different light upon the variation of the water content of zeolites, particularly at lower temperature. Such data as those of Tammann (3) may now be interpreted somewhat differently.

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USE OF THE PHOTOELECTRIC CELL IN THE STUDY OF PHOSPHORESCENCE

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In the course of investigations in this laboratory on the preparation of phosphorescent zinc sulfide, a need arose for a convenient method of measuring luminous intensity of the preparations. While the photometric method has been used extensively in work of this type (1, 2, 5, 7, 8), it was thought that the photoelectric cell might prove adaptable and at once offer possible advantages. Pospielow (4) made photoelectric measurements of the response of phosphorescent materials to cathode rays and ultra-violet light. Schwarz and Urbach (6) have measured the phosphorescence of alkali halides photoelectrically.

Measurements recorded in this paper were made on ZnCuS phosphors all of which were prepared here except samples 1, 2, and 3, which represent commercial materials of the highest grade we could obtain. Our samples were chosen from about one hundred fifty products representing different methods of preparation. So far, we have confined ourselves principally to the problem of measuring response of the phosphorescent materials to excitation by α-particles from a source kept separate from the samples.

APPARATUS

Simple cell-galvanometer hook-up. The Visitron, type F-2, cell generates its own E.M.F., hence the circuit in this case consists of only the cell and a sensitive wall-type galvanometer. Of course, with this type of cell it is important that the galvanometer have low resistance as well as high sensitivity. Our galvanometer had a resistance of 110 ohms and sensitivity of 1.265×10^{-9} amperes. The scale was placed 230 cm. from the galvanometer. The negative terminal of the cell was grounded.

The General Electric P.J.15 cell was used in direct hook-up with a sensitive galvanometer and an E.M.F. of 240 volts.

Amplifier hook-up for P.J.23 cell. The General Electric P.J.23 cell is not sensitive enough to allow satisfactory readings with the simple circuit described above, even for measurement of response to strong α-particle excitation. It was therefore necessary to develop an amplifier for use with this cell (figure 1). In the figure, G_1 is a three-button galvanometer,

G_2 is a Leeds and Northrup type P galvanometer, having a sensitivity of 100 megohms, and L is a 4-dial 10,000-ohm resistance box.

METHOD OF EXCITATION OF PHOSPHORS WITH SEPARATE SOURCE

The samples were spread on 3 in. × 3 in. glass plates. In order to insure uniform thickness and smoothness of surfaces, celluloid strips were held rigidly along two edges of the glass surface while a straight edge was run along the strips, spreading a layer of zinc sulfide about 0.5 mm. thick. The α-particle source was prepared by transferring precipitated radiothorium hydroxide to a 3 in. × 3 in. glass plate and spreading it over a circular area about 3.4 cm. in diameter. The remainder of the surface of the plate was coated with a thick layer of paraffin to keep reflected light from entering the cells. After this deposit had thoroughly dried, it was covered with a layer of collodion and one thickness of cellophane. The strength of the source was between 2 and 3 mg. radium equivalent. The collodion and cellophane served to guard against contamination of the samples and the dark room; however, they reduced the effective strength of the source to about 0.1 its real value.

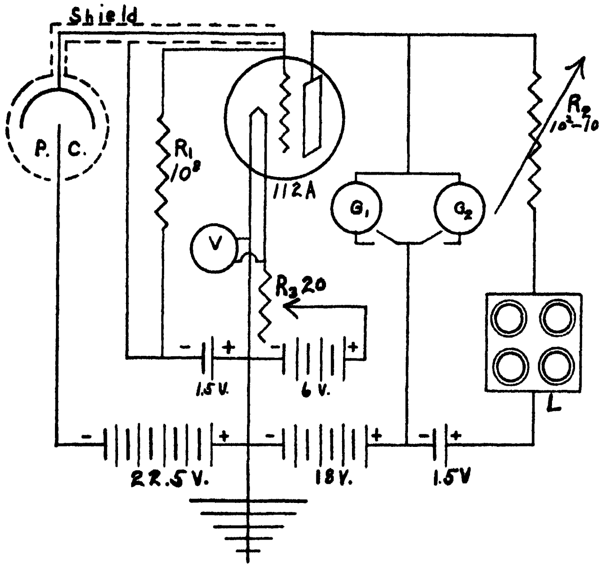

FIG. 1. AMPLIFIER HOOK-UP FOR P.J. 23 CELL

A shallow box was provided with guides on the inside bottom for placing the plates holding the samples so that all had the same position when measured. The source plate was secured, source down, to the under side of a removable shelf which had a centered opening slightly larger than the deposit of radioactive source, through which the light to be measured emerged. When the shelf was placed in position in the box, the α-particle source was directly over the center of the sulfide sample and about 3 mm. distant. Thus most of the measured light passed through the radioactive material, which was not so opaque but that a large part of the emitted light reached the cells. Early measurements disclosed that there was a steady increase in intensity of light up to about ten minutes after the source was placed in position above the samples. Increases after that length of time were so small that any differences of rate of increase among the various samples were negligible. Hence we adopted the procedure of exposing samples to the source ten minutes before making measurements. Care was taken in placing the cells over the opening in the shelf to insure uniformity in exposure of sensitive surface to illuminated area. All measurements were made in the dark room on samples which had been in the dark long enough so that light emission resulting from previous excitation was not appreciable. Because of its convenient form, the Visitron cell was handled in the open. However, in making transfers to and from the shelf, the cell case was not touched on account of the large temperature coefficient of the cell. The P.J.15 cell was permanently mounted in a light-tight box so that the cell was directly over the shelf opening.

TABLE 1

Response of phosphorescent materials to excitation by α-particles

SAMPLE	GALVANOMETER DEFLECTION IN CENTIMETERS			RELATIVE RESPONSE (SAMPLE 1 = 100)			RANK		
	P J 23	F-2	P.J 15	P J 23	F-2	P J. 15	P.J. 23	F-2	P.J. 15
1	22.90	1.90	16.25	100	100	100	3	4	2
2	15.10	1.40	11.80	63.9	73.7	72.6	9	9	5
3	16.70	1.50	13.70	73.0	78.9	84.3	8	8	4
4	16.70	1.60	14.30	73.0	84.2	88.0	6	6	3
5	21.60	2.00	16.80	94.3	105.3	103.4	4	3	1
6	25.50	2.25		111.4	118.4		1	1	
7	23.10	2.05		100.9	107.9		2	2	
8	14.70	1.20		63.8	63.2		10	10	
9	19.10	1.65		83.4	86.8		5	5	
10	16.70	1.50		73.0	78.9		7	7	

Essentially the same arrangement was used for measurements with the P.J.23 cell. The cell was permanently mounted directly over an opening in a shelf which was built into a light-tight box. The source plate was attached to this shelf exactly as described above. Samples were placed in the box under the source by way of a sliding floor which could be slid into and out of the box after raising a sliding door on the side of the box. The shelf and cell were so placed that source and cell occupied the same positions relative to the samples as in the other method. The convenience of this method makes it superior to any other tried.

The results of the measurements are given in table 1.

DISCUSSION OF RESULTS

Measurements with the P.J.15 cell were not completed because of failure of the cell. Exact agreement between the three cells should not be expected, because the samples differ somewhat in color and the cells differ in relative response to different wavelengths of light. In fact, it is surprising that the results show only one discrepancy in ranking. Choice of a cell may be governed by the particular phase of the problem of phosphorescence under consideration. If the problem is comparison of products with a view to use in luminous paint, then the ideal cell would be one whose curve of spectral response coincides with that of the eye. The Visitron cell meets this condition rather satisfactorily, but it does not lend itself well to use with an amplifier, so that one is forced to work with feeble currents. However, the results show that under the conditions of our experiments the currents are large enough for purpose of comparison. Although it is probably safe to assume that measurement of response of phosphorescent material to separate source excitation is a reliable indicator of its usefulness in paint, we plan to extend our method to direct measurement of luminous paints.

By slight modification of the set-up described above for the P.J.23 cell, the photoelectric cell may be used conveniently for measurement of response of the samples to light. We made enough measurements of this kind to confirm the reports of other investigators (3), who have found that response to α-particles cannot be predicted from study of light response.

SUMMARY

1. We have used three types of photoelectric cells in measuring the response of samples of phosphorescent zinc sulfide to α-particle excitation.

2. Difference in spectral response of the cells probably accounts for some differences in results.

3. The photoelectric cell is readily adaptable to measurement of luminous intensity of phosphorescent substances and offers the advantages of simplicity and freedom from the personal element over the ordinary photometric method.

We gratefully acknowledge our indebtedness to Dr. Herman Schlundt, who sponsored this investigation. We are grateful also to Dr. R. T. Dufford for the loan of certain apparatus and to Mr. C. C. Carrol for preparing the radioactive material.

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THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE

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The measurement of the relative solubility of a sparingly soluble salt in a pure solvent, and in the presence of other salts using the same solvent, affords a ready measure of the change in potential or of the activity coefficient of the saturating salt. These changes should be accounted for by any adequate theory of solutions. The interionic attraction theory of Debye and Hückel (2) has achieved considerable success in describing the properties of strong electrolytes in aqueous solutions. The experimental data, using water as a solvent, are quite extensive.

Since the interionic attraction theory is premised on the fact that all effects are due to the electrostatic attraction between ions, it is to be expected that the validity of this assumption and the equations derived by Debye and Hückel (2) could be subjected to a quite rigorous test by employing solvents of lower dielectric constants, since the electrostatic forces between ions vary inversely as the dielectric constant of the medium containing the ions.

The experimental data on the mutual solubility relations in solvents with dielectric constants lower than that of water are limited (1), but cover a range of solvents with dielectric constants ranging from 64 for water at 75°C. (1a) to 6 for acetic acid (1j, 1l). Several types of solvent and saturating salts have been used.

When interpreted in terms of the interionic attraction theory, the results of these investigations are somewhat conflicting. The deviations, as might be expected from the assumptions and approximations made in the development of the equations used, are larger for the solvents of lower dielectric constants and for the higher or more unsymmetrical valence types of salts concerned.

The simple Debye-Hückel equation relating the solubility of a uni-univalent salt to the ionic strength of the solution may be written in the following form:

$$\log \frac{S}{S_0} = \frac{A\epsilon^2\kappa}{2DRT(1 + \kappa b)} - \frac{A\epsilon^2\kappa_0}{2DRT(1 + \kappa_0 b)} \qquad (1)$$

where $K^2 = \dfrac{8\pi\epsilon^2 A\mu}{1000\,DRT}$; S_0 and S are the solubilities (in moles per liter) of the pure saturating salt and of the saturating salt in the presence of solvent salts, respectively; μ_0 and μ the corresponding ionic strengths; A, Avogadro's number; ϵ, the unit charge; D, the dielectric constant of the medium; T, the absolute temperature; R, the gas constant; and b, the mean ionic diameter.

Taking the value of the dielectric constant of acetone at 25°C. as 20.8 (6), substituting the values of the constants, and considering the ions as point charges, equation 1 reduces to

$$\log \frac{S}{S_0} = 3.718\,\mu^{\frac{1}{2}} - 3.718\,\mu_0^{\frac{1}{2}} \tag{2}$$

In equation 2, $\mu_0^{\frac{1}{2}}$ is a constant, hence the equation is linear in $\log \frac{S}{S_0}$ and $\mu^{\frac{1}{2}}$. A plot of $\log \frac{S}{S_0}$ against $\mu^{\frac{1}{2}}$ should yield a straight line with a slope of 3.718 if this simple form of the Debye-Hückel equation holds for solutions of salts in acetone. Solubility measurements of a sparingly soluble salt in acetone will afford a ready means of testing the theory.

MATERIALS

A commercial grade of acetone was dried over anhydrous calcium chloride. Best results were obtained by adding about 35 g. of the anhydrous salt to 1 liter of acetone, and allowing the mixture to stand for about six days with occasional shaking. The acetone, thus treated, was distilled in a vacuum-tight, all-glass still with a fractionating column 125 cm. in length, filled with glass beads. The last third of the distillate was rejected. The distillation was carried out in a darkened room. The product thus prepared showed a density of 0.7845 at 25°C. and an index of refraction of 1.3560 at 25°C., using the D line as standard. Seventy-five per cent of this product distilled in a temperature range of 0.05°C., the entire sample showing a range of 0.10°C.

A standard brand of c.p. sodium bromide was twice recrystallized from distilled water, and dried to constant weight at 300°C. in a current of dry air.

Lithium perchlorate was prepared by the method of Richards and Willard (4). The salt was dried to constant weight by prolonged heating at 150°C. in a current of dry air. The anhydrous salt tested neutral and was free from ferric, calcium, magnesium, potassium, sodium, fluoride, and chloride ions.

Calcium perchlorate was prepared by the method of Willard and Smith (7). The salt was dried to constant weight by heating at 260°C. in a current of dry air. The anhydrous salt tested neutral and was free from ferric, magnesium, and chloride ions.

Every precaution was taken to exclude moisture in the storing and handling of these materials.

METHOD

Half-liter, reground, glass-stoppered flasks were "steamed" with acetone vapor. The required amount of the solvent salt was weighed into the container, and about 450 cc. of acetone was then blown into the flask with a current of dry, carbon dioxide-free air. The weight of the acetone added was noted. After the solvent salt had completely dissolved, a comparatively large excess of sodium bromide was added, after which the glass stopper was sealed in place with a mixture of beeswax and rosin.

The sealed containers were placed in a mechanical shaker and agitated vigorously for from forty-eight to sixty hours, the containers being covered to exclude light. During this period of shaking, the containers were removed several times from the shaker and cooled in an ice bath to expedite the saturation process.

After from forty-eight to sixty hours on the mechanical shaker, the containers were transferred to a constant temperature bath, maintained at 25°C.±0.02°C., and permitted to remain, with occasional shaking, for an additional twenty-four hours.

After equilibrium had been established, as much as possible of the clear supernatant liquid was blown into a weighed flask by a current of dry, carbon dioxide-free air. The weight of the sample was determined, the acetone distilled off over a water bath, and the residue taken up with distilled water.

The sodium bromide present in each sample was determined by the Volhard method (5) for bromide ion estimation.

EXPERIMENTAL RESULTS

The solubility data for sodium bromide in acetone in the presence of lithium and calcium perchlorates are shown in tables 1 and 2, respectively. Figure 1 shows the measured solubility of the sodium bromide as a function of the ionic strength of the solution. The solubilities calculated from equation 2 are also shown. In figure 2, the log $\frac{S}{S_0}$ data from tables 1 and 2 are shown, plotted against the one-half power of the ionic strength. The theoretical lines for acetone (slope 3.718) and for water (slope 0.5) also have been included.

The slope of the best straight line through the experimental points, in the smaller ionic strength region, is about 8.5. Points for the more dilute solutions are closely grouped about this line, indicating that both sets of data give slopes approaching the same limiting slope. The value of the experimentally observed slope is more than twice as large as the theoretical slope for acetone. It would be necessary to assume a dielectric constant of about 10, for the more dilute solutions, to bring the theoretical slope into agreement with the experimental slope.

From equation 1 the slopes, obtained by plotting the log $\frac{S}{S_0}$ values against the one-half power of the ionic strength, for two different solvents, should vary inversely as the three-halves power of the ratio of the dielectric constants for the two solvents, both being at the same temperature. For water and acetone, this ratio is 7.4 at 25°C. The increase in solubility due to a salt with a non-common ion should be 7.4 times greater in acetone than in water. Our experimental data show the increase to be about 17 times greater, which is hardly of the right order of magnitude to be ex-

TABLE 1

The solubility of sodium bromide in acetone at 25°C. in the presence of lithium perchlorate

$LiClO_4$ MOLES PER LITER × 10^3	SOLUBILITY (S) OF NaBr IN MOLES PER LITER × 10^3	$\frac{S}{S_0}$	$\log \frac{S}{S_0}$	$\mu \times 10^3$	$\mu^{\frac{1}{2}}$
0.0000	1.1841	1.0000	0.00000	1.1900	0.03449
0 0000	1 1959				
0.3103	1.3786	1 1585	0.06390	1 6889	0 04109
0.5469	1.4523	1.2204	0 08650	1 9992	0.04471
0.7847	1.5820	1.3294	0.12362	2 3667	0.04865
1 9740	1.9259	1.6148	0 20908	3 8999	0.06245
3.5910	2.2461	1.8875	0.27593	6.1971	0.07872
19.2390	3 5754	3.0045	0.47777	22.8144	0 11790
38.1470	5.2067	4.3754	0.64102	43.3537	0.20823
78.2210	8.2430	6.9269	0.84054	86.4640	0 29405
392.6900	21.5747	18.1300	1.25840	414.2647	0 24363

TABLE 2

The solubility of sodium bromide in acetone at 25°C. in the presence of calcium perchlorate

$Ca(ClO_4)_2$ MOLES PER LITER × 10^3	SOLUBILITY (S) OF NaBr IN MOLES PER LITER × 10^3	$\frac{S}{S_0}$	$\log \frac{S}{S_0}$	$\mu \times 10^3$	$\mu^{\frac{1}{2}}$
0.3057	1.6118	1.3546	0.13182	2 5289	0 05029
0.5535	1 9070	1.6025	0.20480	3.5675	0.05973
0.7716	2.2246	1.8694	0.27170	4.5394	0.06738
1.9680	3.6428	3.0612	0.48589	9.5468	0.09771
4.1290	5.9969	5 0394	0.70238	18.3839	0.13558
8.4210	9.4767	7.9636	0.90111	34.7397	0.18649

pected. The divergence noted here is of the same order of magnitude as that shown by the data of Robinson (1h).

Using equation 1, in which the ionic diameters are not neglected, but only the first terms of the series in the expansion of the hyperbolic sine are

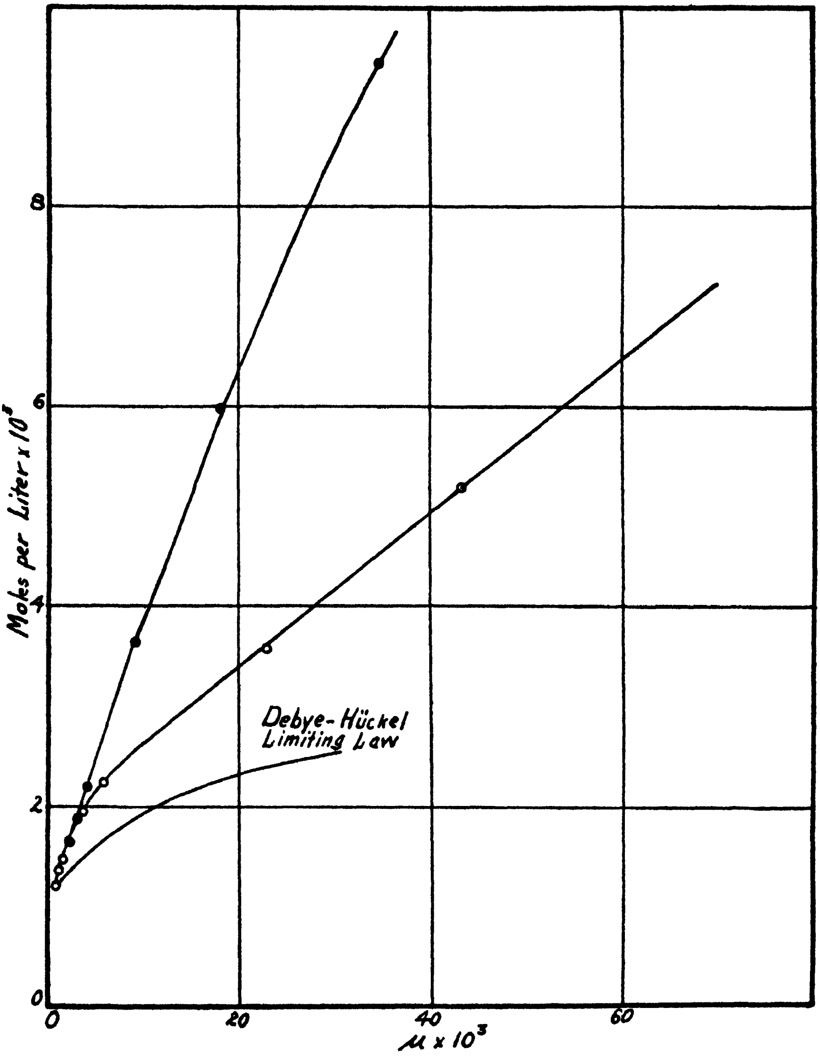

FIG. 1. THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE
○ $LiClO_4$; ● $Ca(ClO_4)_2$

retained, several values for the mean ionic diameter b, were calculated from the experimental data. These values are all negative, the average being about -10×10^{-8}. This corresponds to a value of about 0.5×10^{-8} when the next two terms of the expansion, as developed by Gronwald, LaMer, and Sandved (3), are included. No positive values of the ionic diameter will bring the experimental data and theory into agreement.

We believe that this marked divergence between the theory and experimental results, not only in the case of our data but also in the case of those of Kraus and Seward (1f) and Robinson (1h), is the result of too great a solubility of the saturating salt in acetone. It is reasonable to expect that as the dielectric constant of the solvent becomes smaller, the highest total salt concentration at which the interionic attraction theory will be obeyed must also decrease. Seward and Hamblet (1l) and Scholl, Hutchison, and Chandlee (1j), using glacial acetic acid as solvent (dielectric constant about 6), have found rather good agreement up to a total salt concentration of about 0.0006 mole per liter. In view of this, it appears

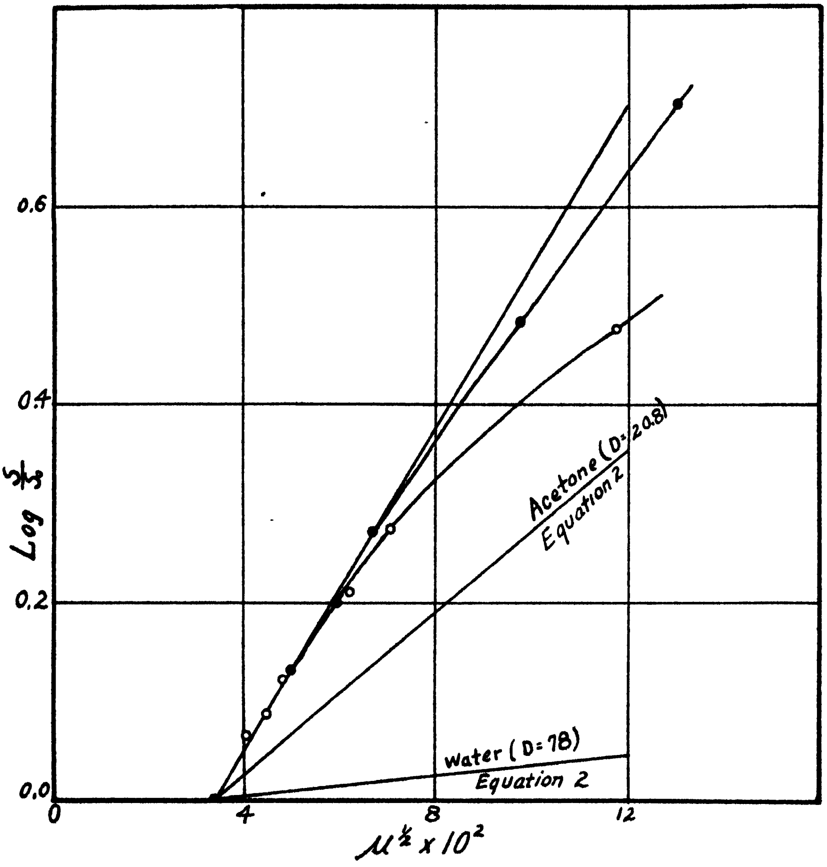

FIG. 2. THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE COMPARED WITH THE INTERIONIC ATTRACTION THEORY

○ LiClO$_4$; ● Ca(ClO$_4$)$_2$

that the total salt concentration should not exceed 0.001 molar, if agreement between the theory and experimental data is to be obtained, using acetone as the solvent.

SUMMARY

The solubility of sodium bromide in acetone, in the presence of lithium and calcium perchlorates, has been determined.

The presence of these solvent salts produces a marked increase in the solubility of the sodium bromide in acetone.

The results have been examined from the point of view of the interionic attraction theory of Debye and Hückel. The observed solubilities are much larger than those predicted by the theory.

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THE SYSTEM ANILINE–FORMIC ACID–WATER

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A study of mixtures of aniline, formic acid, and water was made by the methods commonly used for heterogeneous systems in equilibrium, and the results were summarized in a triangular graph in the usual manner. The region in which the components separated into two liquids was mapped out, and the distribution of the formic acid between the two liquid layers was found. The region in which crystals were deposited was also mapped out, and the crystals were proved to be aniline formate, $C_6H_7N \cdot CH_2O_2$. This work was done at 15°C.

However, these liquid mixtures and also the solid crystals were not in equilibrium; they changed continuously, producing formanilide and water. Thus crystals first formed in a given system of the components redissolved; and liquid mixtures at one time homogeneous, in time separated into two layers. Moreover the crystals of aniline formate were unstable in two directions, dissociating into aniline and formic acid on the one hand and giving formanilide and water on the other.

Goldschmidt and Wachs (3) studied the rate of formation of anilides, proving it to be in general bimolecular, while Davis and Rixon (2) studied the equilibrium, formic acid + aniline $\rightleftarrows$ formanilide + water, in a solution of aqueous pyridine at 100°C., but they do not mention aniline formate. This equilibrium was confirmed in the course of the present work. Also a study of some properties (density, etc.) of certain mixtures of these three components was made by Pound and Russell (5).

The aniline was purified by distillation. The formic acid–water solutions, containing from 5 to 87 per cent formic acid, were made from the best commercial acids, 40 per cent and 87 per cent; from the latter acid, by treatment with the calculated amount of phosphorus pentoxide and by subsequent distillation *in vacuo*, there was obtained the 99 per cent acid, (see ref. 4). The formic acid content of these solutions and of the mixtures was found by titration with standard baryta water, using phenolphthalein; with this process the presence of aniline or of formanilide did not interfere. Such direct titrations of the mixtures gave the free formic acid and the acid present as aniline formate, the latter evidently dissociating in the process; such formic acid will be referred to as "free acid." By boiling solutions containing formanilide with an excess of caustic soda and then cooling and titrating with acid, the "total acid" was obtained, i.e., formic acid free and as aniline formate and as formanilide. The difference, "total acid" – "free acid," or "fixed acid," gave the formic acid fixed as formanilide. "Fixed acid" was also obtained in the solution after the neutralization of the "free acid" by boiling with excess caustic soda, etc., and this procedure gave the same results as the former.

Aniline was determined in the mixtures by titrating the warm acidified solutions containing potassium bromide with potassium bromate solution, using starch–potassium iodide as outside indicator; the bromate solution was standardized against pure aniline. This method gave the total aniline in the mixture, i.e., aniline free and as formate and as formanilide.

TABLE 1

FORMIC ACID USED	COMPOSITION OF THE CRITICAL MIXTURE		
	Aniline	Formic acid	Water
per cent	*per cent*	*per cent*	*per cent*
5.164	13.55	4.45	82.0
9.73	21.7	7.6	70.7
12.91	34.65	8.45	56.9
16.17	50.1	8.1	41.8
20.29	67.05	6.7	26.25
22.79	78.7	4.85	16.45
	95.09		4.91
	3.61		96.39

The percentages (weight) of aniline, formic acid, and water will be referred to as per cent aniline, per cent formic acid, and per cent water. Per cent formic acid without qualification means per cent of "free acid" (as defined above).

I. DETERMINATION OF THE UNOBTAINABLE LIQUID MIXTURES, I.E., OF THE LINE *BSSC*

This was got by the direct titration of the following formic acid solutions by aniline. The critical mixture, shown by characteristic opalescence, could be found to within a drop of aniline, the total amount of which varied from 5 to 40 cc. (see table 1). The critical mixtures of aniline and water were taken from Applebey and Davies (1), and from other workers (see ref. 6). The above critical mixtures are marked ☐ in the graph.

II. THE DISTRIBUTION OF THE FORMIC ACID

The distribution of the formic acid between the aniline and the aqueous layers gave the following results:

	per cent formic acid in aniline layer	*per cent formic acid in aqueous layer*
From 5.164 per cent formic acid	0.65	4.0
From 9.73 per cent formic acid	1.45	5.75
From 20.29 per cent formic acid	3.75	7.1

The three resulting tie lines are drawn in the graph.

III. DETERMINATION OF THE CURVE *DPG*

The curve *DPG*, bounding the region in which crystals separated, was determined by three methods:

a. Mixtures were made up from known weights of aniline and of formic acid solutions, and the resulting crystals and solutions were agitated in a thermostat at 15°C. for ¾ hour or more, and then separated and analyzed for "free acid" and aniline. The crystals were needle-shaped and long, especially if formed slowly or on the sides of the vessel above the main mixture. Rapid mixing gave small and entangled crystals and a semisolid mass which disentangled on agitation. On long agitation squat and compact crystals sometimes took the place of the needles. Both these kinds of crystals were aniline formate (see later). On further agitation the crystals in some experiments disappeared altogether.

TABLE 2

COMPOSITION OF SOLUTION			COMPOSITION OF CRYSTALS		
Aniline	Formic acid	Water	Aniline	Formic acid	Water
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
79.6	7.2	13.2	68.7	29.5	1.8
64.8	11.3	23.9	66.9	30.4	2.7
51.9	12.5	35.6	63.2	29.9	6.9
38.5	18.4	43.1	64.0	31.8	4.2
36.8	24.0	39.2	61.1	31.4	7.5
35.1	33.1	31.8	60.6	32.7	6.7
38.1	41.1	20.8	62.7	33.6	3.7

The method of residues was used thus to give the points on the curve *DPG* and the tie lines leading to the point *H*, representing aniline formate. The results were only approximate: long agitation meant that much formanilide was formed, which of course vitiated the result, and short agitation meant that the solution and crystals had not perhaps reached equilibrium at 15°C. Mixtures of aniline with the more concentrated formic acids were the most affected by the former complication, but all of the results were somewhat so affected. Hence especially the percentage of free acid in the solutions was lower than it should have been. A few typical results were those given in table 2. These points are marked ○ in the graph.

b. Various formic acid solutions were titrated by aniline, at 15°C., until crystals permanently remained in the mixtures. This method gave points along the curve *PG*. These crystals were squat. The points obtained in this manner probably tend to lie below the true solubility curve, i.e., crystals appeared momentarily as the aniline was run in and subsequently did not dissolve within a short time. When the 99 per cent formic acid was thus titrated with aniline, crystals remained when the mixture contained 34.4 per cent aniline,—obviously low. By taking aniline formate and finding the amount of 99 per cent acid which would just dissolve it, the point *G* was found at 37 per cent aniline,—a value which is still probably low. Thus 10 cc. (11.87 g.) of 76.08 per cent formic acid required 6.86 cc. (7.07 g.) of aniline, and the mixture then contained 37.3 per cent of aniline. It was found that for crystals to persist in the mixtures the following percentages of aniline were required:

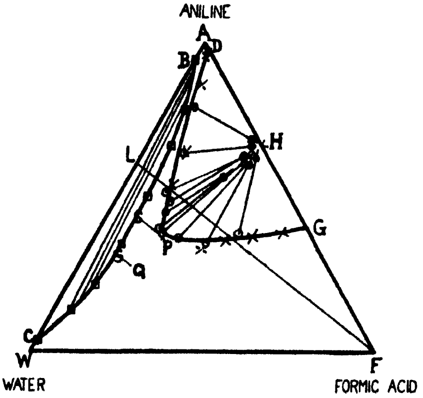

FIG. 1. THE SYSTEM ANILINE–FORMIC ACID–WATER

48.9 per cent formic acid solution required 33.2 per cent aniline
61.44 per cent formic acid solution required 35.9 per cent aniline
76.08 per cent formic acid solution required 37.3 per cent aniline
87.23 per cent formic acid solution required 38.2 per cent aniline

These points are marked × in the graph.

c. Aniline was titrated with various formic acid solutions at 15°C. until crystals persisted in the mixtures. Thus points along the curve *DP* were obtained. The crystals formed were generally needle-shaped. Thus 28.7 g. of aniline take 1.00 g. of 48.9 per cent formic acid solution, and the per cent of aniline in the mixture is thus 96.6. The mean results indicate that for crystals to persist in the mixtures the following percentages of aniline were required:

30.5 per cent formic acid solution required 54.2 per cent aniline
35.67 per cent formic acid solution required 65.1 per cent aniline
43.8 per cent formic acid solution required 86.9 per cent aniline
48.9 per cent formic acid solution required 96.1 per cent aniline
76.08 per cent formic acid solution required 97.9 per cent aniline

These points too are marked × in the graph.

IV. CHANGES IN THE LIQUID MIXTURES ON KEEPING

Mixtures containing appreciable formic acid and water showed a pink color on addition of the aniline; this increased in intensity for a few minutes and then decreased after ten minutes or more.

Mixtures of the three components were kept for many days at room temperatures, about 10°C., some in stoppered flasks in desiccators, others in sealed tubes; they were analyzed from time to time. In all of them the "free formic acid" plus the "fixed formic acid" equalled the original "free formic acid." The "free acid" decreased roughly in accordance with the bimolecular action, i.e., the formic acid fixed as formanilide in a given time was roughly proportional to the product of the aniline and formic acid percentages (concentrations). Moreover the speed of this action rapidly increased as the water-content decreased; a lowering of the water by about 14 per cent trebled the speed of action, other conditions being equal. Also a state of equilibrium was obtained after ten days or so, if the solution remained homogeneous; no satisfactory equilibrium constant was obtained however. A few typical results are given in table 3.

The formation of formanilide may be taken as equivalent to adding more aniline to the mixtures. Thus a mixture originally containing p per cent aniline, q per cent formic acid, and r per cent water, when the per cent of free formic acid falls to $(q - x)$, becomes $(p - 2.02\,x)$ per cent aniline, $(q - x)$ per cent formic acid, $(2.63\,x)$ per cent anilide, and $(r + 0.39\,x)$ per cent water, which behaves as $(p + 0.61\,x)$ per cent aniline, $(q - x)$ per cent formic acid, and $(r + 0.39\,x)$ per cent water, or the mixture moves to states along lines parallel to PS and QS, i.e., parallel to the line from the formic acid corner to the (61 per cent aniline, 39 per cent water) mixture, FL. Thus mixture P, No. 27, on the eighth day when it had just separated, contained only 8.6 per cent "free acid," and thus the "fixed acid" was 10.6 per cent, which was equivalent to 21.4 per cent of fixed aniline, as 27.9 per cent of anilide, and to 4.15 per cent of extra water; and the mixture then contained 8.6 per cent of "free acid," 15.8 per cent of free aniline (the dissociable aniline formate being included in these figures), with 27.9 per cent of anilide and 47.7 per cent of water; this mixture behaved as one with 8.6 per cent formic acid, 43.7 per cent aniline, and 47.7 per cent water, and therefore separated into two layers.

TABLE 3

NO.	MIXTURE			FORMIC ACID OBTAINED AFTER TIME GIVEN	
	Aniline	Formic acid	Water	Time	Formic acid
	per cent	*per cent*	*per cent*	*days*	*per cent*
3	19.95	39.15	40.9	35	30.9
				61	31 0
				71	30 9
6	25.65	36.35	38.0	40	25.3
				68	25.4
10	26.75	35.82	37.43	$\frac{1}{24}$	35 26
				$\frac{7}{8}$	29 93
				2	27.2
				4	24.8
				9	24 21
				27	24.17
				34	24.18
				42	24.18
				63	24 28
				74	24 27
24	9.15	4.69	86.15	2	4.20
				8	4 13
				16	4 02
				26	3 92
25	19.8	10.36	69.85	2	9.96
				8	8 64
				11	8 16
				14	Separated
26	28.0	14.6	57.4	2	12 9
				8	9 44
				9	Separated *QS*
27	37.2	19.2	43.6	2	14.25
				8	8.58, separated *PS*
31	78.65	5.35	16.0	2	4.11, separated
32	39.7	52.6	7.7	$\frac{1}{8}$	46.5
				2	36.9
				9	34.4
				17	34 1
				30	34 12

TABLE 3—*Concluded*

NO.	MIXTURE			FORMIC ACID OBTAINED AFTER TIME GIVEN	
	Aniline	Formic acid	Water	Time	Formic acid
	per cent	*per cent*	*per cent*	*days*	*per cent*
35	20 3	49 0	30 7	2	44.8
				9	41 5
				17	41 0
				30	40.0
39	18.9	70.7	10.4	$\frac{7}{8}$	68 5
				4	65 5
				11	63.1
				16	62.7
				25	62 66

Undoubtedly this hypothesis was in general accordance with the facts observed. Thus mixtures like Nos. 3, 6, 10, 32, 35, and 39 came to equilibrium and never separated into layers; mixtures near the line *BSSC*, like Nos. 31, 25, 26, 27, soon separated, and at points *S* as calculated above. Mixtures within the area *DPG* formed crystals, which dissolved in time, and these mixtures then separated in a similar manner to the former ones. Mixture No. 24 shows the influence of water, and mixture No. 31 that of aniline, on the rate of change, on the equilibrium, and on the final separation into two layers.

V. THE CRYSTALS, ANILINE FORMATE, AND THEIR CHANGES ON KEEPING

The crystals of aniline formate were not readily soluble in benzene, toluene, carbon tetrachloride, or petrol; they readily dissolved in water, methyl and ethyl alcohols, acetone, ethyl acetate, chloroform containing 2 per cent alcohol (B.P. chloroform), and in ether. They recrystallized as the ether evaporated. The crystals when kept beneath petrol soon became brown, and simple washing with petrol made them brownish. The white crystals remained unchanged beneath toluene for a few days, but then changed rapidly and soon a brown liquid, aniline or formanilide, was left. When kept in the air or dried in a current of air, the crystals acquired a pinkish or yellowish or brownish tinge.

Many samples of these crystals were made and were washed with one or other of the first four solvents, dried in desiccators over sulfuric acid or calcium chloride, and examined from time to time. Two white samples of the acicular crystals, analyzed at once, both gave 33.2 per cent formic acid and 66.1 per cent aniline, thus per cent of moisture by difference was 0.7; another sample gave 33.8 per cent formic acid, but smelt of free formic acid. Theoretically aniline formate contains 33.1 per cent formic acid and 66.9

per cent aniline. When dry crystals of the aniline formate were kept over sulfuric acid, the smell of formic acid could be detected after some hours and aniline could be detected in the sulfuric acid after some days. The dissociation into aniline and formic acid is therefore appreciable at room temperatures.

The crystals were usually in long needles, but (see above) occasionally there were obtained more compact forms (squat monoclinic prisms); these had the same composition as the needle-shaped crystals. Microscopic examination of freshly formed samples of the crystals indicated the presence of some compact crystals along with the main mass of acicular crystals. These last apparently changed the more quickly (surface effect?), leaving the compact forms. A second crop of crystals formed from a mixture of formic acid and aniline also tended to consist of compact forms.

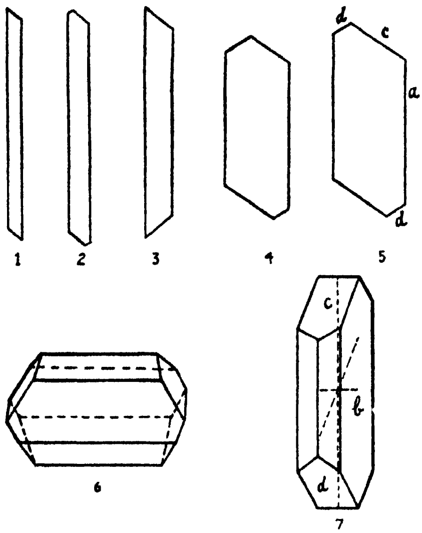

Fig. 2. Crystals of Aniline Formate

The authors owe thanks to Mr. H. Yates, who examined and sketched these crystals and who supplied the following notes on the accompanying sketches (figure 2): "In the graph the figures 1, 2, and 3 are various shapes of acicular crystals, showing three types of crystal-face, of which two are developed in 1, and all three in 2, while in 3 the vertical faces are fully developed but there is only one of each type of inclined face. Crystal 1 was actually seen to grow into form 2 by developing of the third type of face. The angle between the two faces in 1 is 52°.

"Figures 4 and 5 represent tabular crystals lying on the clino-pinacoid plane. From these shapes the interfacial angles are: ac = 57°20′; ad = 59°; cd = 63°40′.

"Figure 6 is an actual sketch of a typical prismatic crystal under the microscope.

"Figure 7 is the same crystal correctly oriented, showing its monoclinic symmetry and the positions of the crystallographic axes."

The melting point of the crystals was 62°C. (maximum value), with average values about 60°C. The values varied as might be expected; also a remelting was always at a lower temperature than the original.

The crystals on keeping gradually became sticky; then very small crystals above or apart from the main lot became yellowish and liquefied; in a sealed vessel after several days a film of liquid (droplets) could be seen between the crystals on the walls of the vessel. Then the stickiness increased and the sample became yellowish or brownish, and finally free liquid (solution) accumulated, and in a couple of days more the crystals had disappeared. These changes took in all about seventeen days in a closed vessel at room temperatures (about 10°C.).

The petrol-washed samples changed very quickly. One such sample after nine days over calcium chloride had formed a yellowish liquid, and after twenty-four days a brown liquid; after sixty days new crystals had formed. The liquid was drained from these crystals, which were then washed and recrystallized from xylene; they gave a melting point of 43°C., indicating that they were (impure) formanilide (m.p. = 46°C.).

The crystals kept in contact with the mother liquor changed the fastest of all; they took but two or three days to disappear.

Many samples of crystals were kept in sealed vessels or over various drying agents and other reagents, but the changing to liquid was never stopped, though it might have been retarded by the absence of moisture. The free formic acid content diminished, and the fixed formic acid content increased continuously. In general, the (free *plus* fixed) formic acid in old crystals equalled the original free acid; in some samples there may have been some adsorption of water, and in other samples some preferential loss of formic acid over loss of aniline; but the loss of acid by volatilization was insignificant as compared with loss of acid by change into formanilide. Thus the crystals A (see table 4) gave a final liquid containing 7.3 per cent of free acid and 25.1 per cent of fixed acid; total = 32.4 per cent, original = 32.2 per cent. The crystals O gave on the fourth day 32.7 per cent of free acid and 1.0 per cent of fixed acid; total = 33.7 per cent, original = 33.8 per cent. The crystals L, from the third experiment reported in section IIIa, gave a final liquid containing 4.7 per cent of free acid and 26.9 per cent of fixed acid; total = 31.6 per cent, original = 29.9 per cent. However they were put in a desiccator overnight before sealing. After nine days crystals N were nearly all liquefied, and the sample went 16.2 per cent of free acid, 8.4 per cent of fixed acid,—indicating that much water had been picked up; the outer water contained both aniline and formic acid. Allowing for the water picked up, the rate of fixation of acid as formanilide was found to be the same as for the first six days.

The free acid content of some samples of crystals kept at room temperatures varied as shown in table 4.

TABLE 4

CRYSTALS WASHED WITH	SAMPLE	CONDITION OF KEEPING	ORIGINAL PER CENT FORMIC ACID	AFTER DAYS	PER CENT FORMIC ACID	FINAL STATE	CHANGE IN PER CENT FORMIC ACID PER DAY
CCl_4, petrol, and dry air	A	In sealed tube	32.2	12	7.3	Liquid	2.08
	B	Over $CaCl_2$	32.2	12	24.1	Quite sticky	0.68
CCl_4, toluene, and dry air.	E	In sealed tube	34.6	6	11.7	Liquid	3.8
	C	Over H_2SO_4	34.6	14	9.3	Two-thirds liquid	1.8
	D	Over P_2O_5	34.6	14	15.2	One-third liquid	1.4
CCl_4 and dry air..	F	In sealed tube	32.5	13	7.9	Liquid	1.9
	G	Over H_2SO_4	32.5	13	28.8	Sticky	0.28
	H	Over KOH	32.5	13	27.3	Sticky	0.40
Toluene, CCl_4, and dry air.....	O	In air	33.8	6	32.5	Slightly sticky; yellowish	0.22
	N	Over water	33.8	6	26.2	Very moist; white	1.25
	M	Over NaOH solution	33.8	6	26.4	Quite moist; white	1.2
	Q	Over $CuSO_4$	33.8	6	29.6	Sticky; brownish	0.7
	R	Over H_2SO_4	33.8	7	32.2	Slightly sticky; white	0.23
	P	Over P_2O_5	33.8	6	—	Slightly sticky; white	—
			33.8	9	31.2	Slightly sticky; white	0.29
Toluene..........	K	In sealed tube	33.0	15	7.2	Liquid	1.7
(Only drained from liquor)....	L	In sealed tube	29.9	24	4.7	Liquid	1.05

The samples A, E, F, K, and L had just liquefied completely in the time shown. This liquefaction took, on the average, seventeen days, and then the per cent of free acid had fallen to the average value of 6.2 (seven samples). The original condition of the crystals evidently had an influence on their subsequent rate of change. Possibly the presence of excess of formic acid in the crystals E, C, and D accelerated their changing. Also the crystals passed to liquid and lost more free acid in sealed vessels than in the open air. The average loss in per cent of free acid, excluding samples C, D, and E, in sealed samples was 1.6 per cent per day (seven samples); in samples over sulfuric acid, 0.22 per cent per day (five samples); and in samples over calcium chloride, 0.66 per cent per day (three samples). The drier the atmosphere about the crystals the slower seemed to be the rate of change of free acid, but even with excess of phosphorus pentoxide, as in sample P, the characteristic changing to formanilide still went on. The crystals, apart from the consequences of this changing, did not appear to be deliquescent.

In conclusion, the crystals of aniline formate change according to both the reactions:

$$\text{Aniline} + \text{Formic acid} \underset{(1)}{\rightleftharpoons} \text{Aniline formate} \underset{(2)}{\rightleftharpoons} \text{Formanilide} + \text{Water}$$

Probably change 2 is accelerated by water and by formic acid (see ref. 2); this change indeed may only occur in solution. Moreover as the products of the dissociation 1 may both provide such a solvent and are also both hygroscopic, the difficulty of stabilising the compound, aniline formate, will be realized.

SUMMARY

1. The authors have studied the behavior of mixtures of aniline, formic acid, and water at room temperatures.

2. The region of partially miscible mixtures has been mapped out.

3. The distribution of formic acid between the aniline and the aqueous layers has been found.

4. The region in which crystals of aniline formate separated has been mapped; no other solid phase was found.

5. The change of the liquid mixtures into formanilide was studied.

6. The change of the solid crystals of aniline formate into formanilide was studied.

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INTERMITTENCY AND THE HERSCHEL EFFECT[1]

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DISCUSSION

Many hypotheses have been advanced to explain the effects produced by exposure of photographic emulsions to radiant energy. One of the more fruitful of these hypotheses assumes that the action of light on the photographic emulsion is photochemical, and postulates the coëxistence of forward and reverse reactions. The forward reaction causes the silver halide grains in the emulsion to pass from the original undevelopable state to a developable state. The reverse reaction causes the exposed grains to return to an undevelopable state somewhat similar to that which existed before exposure. When light falls on the emulsion, the forward process causes grains to become developable. As soon as an appreciable number of grains becomes developable, the reverse reaction causes some of them to become undevelopable. After the exposure has proceeded for some time, a statistical equilibrium between the two reactions may be reached when just as many grains are being made undevelopable as are being made developable.[2] This condition corresponds to the horizontal portion of the characteristic time–density curve, that is, the portion of the curve where further exposure produces no further increase in density.

The magnitude of the equilibrium density attained on any given emulsion is a function of the wavelength and intensity of the radiation. In general the greater the intensity of the incident illumination, the greater will be the resulting equilibrium density. The effect of the wavelength of the incident radiation is dependent on the spectral sensitivity of the emulsion. Exposure to blue light produces high developable density on ordinary chloride emulsions, while orange or red light produce low developable densities. It seems then that with blue light the forward reaction greatly predominates over the reverse reaction, while with red light this predominance is not so great. If an emulsion is given an exposure to blue light sufficient to produce a relatively high developable density and is subsequently given an exposure to red light, the density produced by the first exposure may be somewhat reduced by the second. This reduction in developable density by reëxposure to light of the longer wavelength is known as the Herschel effect. By means of the above considerations the Herschel effect may be explained[3] as being brought about by predominance of the reverse reaction during the exposure to red light.

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[1] Paper read before the Twelfth Midwest Regional Meeting of the American Chemical Society, held at Kansas City, Missouri, May 3, 1934.

[2] The system of reactions occurring when energy falls on a photographic emulsion is not always as simple as that outlined above. It has been shown that developable grains are not always capable of being returned to an undevelopable state by the reverse reaction. Such grains are said to be in a "non-reversible state." The amount of non-reversible density existent at any one time appears to be a function of the total developable density concomitantly existent. We hope to discuss this relationship and its implication more fully in a future paper.

Numerous studies have been made of the relative efficacy of continuous and intermittent primary photographic exposures. Intermittent exposures, to the same illumination and for the same effective length of exposure time, have been found in general to be less effective in producing density than continuous exposures, although it has been found that for exposures to extremely high light intensities and for very short intervals of darkness, intermittent exposures may be more efficient than continuous exposures in building up density. This difference in the density produced by intermittent exposures and by equivalent continuous exposures is known as the intermittency effect. As with the Herschel effect, the intermittency effect may be explained on the hypothesis of simultaneous forward and reverse reactions if we also assume the existence of photochemical lags in these reactions (1, 2, 3).

EXPERIMENTAL

It is supposed that, when the illumination is interrupted,—as it is during the periods of darkness in intermittent exposure,—a definite interval of time must elapse before the two reactions cease. Upon this hypothesis Blair and Hylan have suggested that those factors which accentuate the forward reaction, such as (1) strong illumination, (2) short wavelength, and (3) fast emulsion, should make an intermittent exposure more efficient than a continuous one. They also suggest that those factors which accentuate the reverse reaction, such as (1) faint illumination, (2) long wavelength, and (3) slow emulsion, should make an intermittent exposure less efficient than a continuous one. These suggestions are in keeping with experimental data. Intermittent exposures usually produce less developable density than do equivalent continuous exposures. This fact is explained by supposing that the terminal lag of the reverse reaction predominates over that of the forward reaction.[4] The result, then, is that the density which has been built up during the period of exposure is reduced slightly during the period of darkness. That is, density is not built up at so great a rate by intermittent exposure as by continuous exposure. Moreover, the equilibrium density resulting from intermittent exposure is less than that resulting from continuous exposure.

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[3] For an historical summary and bibliography of the concept of the Herschel effect as a regression phenomenon, see Lüppo-Cramer (Proc. 7th Intern. Congr. Phot. (London), p. 45 (1928)). For a more precise treatment, see Joehnck and Blair (J. Optical Soc. Am. **23**, 67 (1933)), James (J. Chem. Physics **2**, 132 (1934)), and the forthcoming paper mentioned in footnote 2.

Factors which accentuate the reverse reaction, such as faint illumination, long wavelength, and slow emulsions, tend to produce a reduction of density during the periods of darkness in intermittency. It is ordinarily necessary that these same conditions be present in order that the Herschel effect may be produced. These considerations enable us to predict that, when the above-mentioned factors are present, intermittent exposures will be more effective in producing the Herschel effect than equivalent continuous exposures.

In order to test the above-mentioned prediction, a series of experiments was made on a slow, contrasty emulsion which is particularly subject to the Herschel effect (Azo F No. 5 paper). The paper was exposed to white light from an incandescent lamp for 48 seconds, the energy intensity at the surface of the paper being 1550 ergs per square centimeter per second. This exposure produced a high developable density approximating that shown on the ordinate at $t = 0$ in the figures. Successive sheets of the exposed paper were then reëxposed, some intermittently and others continuously, to a second radiation of intensity 1700 ergs per square centimeter per second. The intermittent exposures were made in a sensitometer employing a sector wheel of 120 degrees opening and rotating at a speed of 28 R.P.M. Three separate wavelength bands of secondary radiation, as given by appropriate Wratten filters, were employed,—orange, red, and short infra-red. The filters employed were No. 72 (600 and 700 mμ), No. 70 (700 mμ), and No. 88 (over 700 mμ). Each filter was used in conjunction with a water-cell which passed 90 per cent of radiation of wavelength 800 mμ, 50 per cent of 900 mμ, and only 10 per cent of 1000 mμ. The sheets were developed for 90 seconds in (Eastman formula) "D-73" developer (diluted 1 part of developer to 3 of water) at 21°C., fixed in acid hypo, washed, and ferrotyped. The normal reflection densities remaining after stated reëxposure intervals were measured with a photoelectric cell reflection densitometer.

The results are depicted in figures 1, 2, and 3, where the normal reflection densities are plotted against the corresponding intervals of exposure to the "herschelizing" light. It is apparent from the figures that intermittent exposure, under the conditions of the experiment, produces a relatively greater Herschel effect than corresponding intervals of continuous exposure to the "herschelizing" light. There is not sufficient data at hand to enable any explanation of why the observed "spread" between the curves for intermittent and for continuous exposure is apparently greater for orange light than for the longer wavelengths. This variation of "spread" with wavelength was found in all of several different determinations.

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[4] Davis (2) suggests that, during the period of the terminal lags, the "strength" of both the forward and reverse reactions falls off exponentially, so the resultant effect is a difference between two exponential functions.

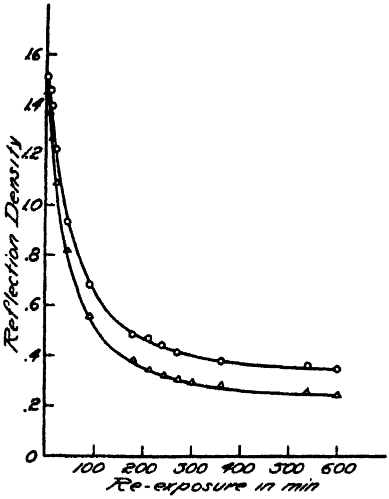

FIG. 1. INTERMITTENCY AND THE HERSCHEL EFFECT IN ORANGE LIGHT
O, continuous reëxposure; △, intermittent reëxposure

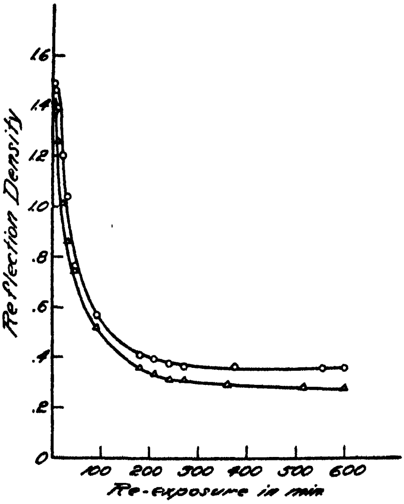

FIG. 2. INTERMITTENCY AND THE HERSCHEL EFFECT IN RED LIGHT
O, continuous reëxposure; △, intermittent reëxposure

Though perhaps not apparent from the extent of the curves, there seems to be a tendency for prolonged infra-red exposure to yield slightly lower equilibrium densities than those obtaining for orange light. In any event absolute density comparisons, for much prolonged exposure times and for low densities, are rendered difficult both by natural regression of the latent image with time (in the dark) and because of the fact that at low densities variations introduced by slight differences in development conditions are relatively more important than at higher densities.

SUMMARY

The interpretation of the Herschel and intermittency effects is briefly discussed on the basis of the familiar hypotheses of simultaneous forward and reverse reactions with accompanying photochemical lags. From a consideration of certain implications of these hypotheses a new effect is predicted. The existence of this effect—namely, that intermittent exposure to the "herschelizing" light will be more efficient in producing Herschel effect than equivalent continuous exposure—has been amply proven by laboratory results employing three different wavelength bands of "herschelizing" light.

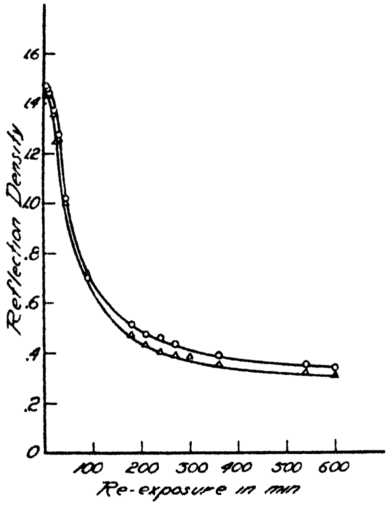

FIG. 3. INTERMITTENCY AND THE HERSCHEL EFFECT IN INFRA-RED LIGHT
○, continuous reexposure; △, intermittent reëxposure

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A STUDY OF THE BENZOIN REACTION. I

THE REACTION BETWEEN PURE BENZALDEHYDE AND PURE POTASSIUM CYANIDE

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INTRODUCTION

Smith (8) in 1899 stated that potassium cyanide and benzaldehyde yield benzoin in the absence of water. This statement was later contradicted by Lachmann (4), who considered that Smith's experiments had been vitiated by contamination with atmospheric moisture. More recently Morton and Stevens (7) have again stated that water is unnecessary for the production of benzoin.

This discrepancy in the published results on the place of water in the benzoin reaction is important, as the most widely accepted view of the mechanism of the reaction (6) involves the formation of a cyano ion. In addition an insight into the innate nature of the benzoin reaction may be obtained by a study of the kinetics of the heterogeneous reaction between alkali cyanide and benzaldehyde, assuming that the reaction can proceed in the absence of all solvents and reagents.

ANALYTICAL METHODS

The method used by Stern (9) is accurate, but not rapid. The methods of Lachmann (5), Morton and Stevens (7), and Anderson and Jacobson (2) are not sufficiently accurate, as they make no allowance for the solubility of benzoin in benzaldehyde even in the presence of water. Ten grams of wet benzaldehyde dissolve about 0.9 g. of benzoin. As a result of a number of control experiments the following technique was finally standardized.

The reaction mixture from 10 g. of benzaldehyde and varying amounts of cyanide is treated with 20 cc. of glacial acetic acid, and warmed until solution is complete. The liquid is then mixed with 35 cc. of water and allowed to stand overnight to ensure complete separation of benzoin. This is filtered off, dried, and weighed. Benzaldehyde is extracted from the filtrate with ether, and the extract dried over calcium chloride. The liquid after removal of ether is distilled at 2 mm. pressure at 110°C. The solid residue is dissolved in 10 cc. of glacial acetic acid, which is then diluted with 100 cc. of water. The precipitated benzoin is filtered off after twelve hours, dried, and weighed.

The benzoin as weighed was relatively pure, having a melting point not lower than 129°C. Little side reaction occurred under the conditions of the experiments, as may be seen from the high yields on prolonged heating (figure 1) and from the fact that the benzoin did not lose weight on extraction with sodium carbonate solution, showing the absence of benzoic acid.

MATERIALS EMPLOYED

Benzaldehyde

Kahlbaum's "purest" benzaldehyde was first used. It was confirmed that the experimental results were not altered when this benzaldehyde was washed with sodium carbonate solution, dried over calcium chloride, and distilled in a current of nitrogen which had been treated with pyrogallol solution, soda lime, and sulfuric acid. Merck's "purest" benzaldehyde gave identical results in trial experiments and was also used. Technical benzaldehyde, even when purified by washing with alkali and with water followed by distillation in a current of pure nitrogen after drying, gave variable results.

The sensitiveness of the benzoin reaction to traces of impurities in the benzaldehyde used has been commented on by Stern (9). Slight contamination of the hydrogen in which the benzaldehyde was distilled inhibited the reaction. The nature of the impurity was not traced, but it may have been hydrogen sulfide.

It is essential that the benzaldehyde should be free from benzoic acid, since this directly attacks the cyanide (1). To avoid oxidation, the aldehyde was stored in small lots in an atmosphere of purified nitrogen.

The formation of acid in any lot was detected by a fall in the yield in check experiments. Quinol cannot be used to inhibit oxidation as it is a negative catalyst for the benzoin reaction (see Part II[1]).

Potassium cyanide

Kahlbaum's or Merck's "purest" potassium cyanide was used. As received, these cyanides contained traces of moisture, but after drying at 110°C. at 2 mm. for 2 hours (11) analysis showed 100 ±0.05 per cent potassium cyanide. The dried material was stored in small lots out of contact with carbon dioxide and water, and was weighed in a closed bottle.

EXPERIMENTAL METHODS

The benzaldehyde was weighed in a closed bottle and poured into the glass reaction bottle, an allowance, experimentally determined, being made for the benzaldehyde adhering to the sides of the weighing bottle. The reaction bottle was previously washed with pure acetone and with distilled water and heated at 107°C. in an oven; the bottle had a heat capacity such that on adding the benzaldehyde its temperature fell close to 100°C.

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[1] To appear in the next issue.

Immediately the benzaldehyde had been poured in, the necessary amount of potassium cyanide was added, and the reaction bottle sealed with a glass stopper, a rubber washer, and a spring clip. Each washer was thoroughly cleaned with acetone and distilled water before use, and was discarded after it had been used thrice.

The sealed bottle was shaken in a thermostat at two vibrations per second at 100 ± 0.2°C. The time of shaking was controlled by a stop watch.

No difficulty was experienced in repeating experiments to within 0.1 g. benzoin.

SOLUBILITY OF POTASSIUM CYANIDE IN BENZALDEHYDE

Experiments have shown that benzaldehyde even at 100°C. does not dissolve potassium cyanide (cf. Stern (9)).

SOME PRELIMINARY EXPERIMENTS

A number of experiments were made to examine the effect of certain external factors on the course of the reaction. It was found that the rate of reaction was not affected by addition of ground glass, by increasing the rate of shaking, or by using a sealed reaction vessel of thin glass which was previously evacuated at 2 mm. pressure. It can be concluded therefore that the reaction was not affected by the glass surface nor by the rubber washer, nor by the presence of air in the reaction vessel.

It should be emphasized that in spite of these experiments there is present a constant factor which poisons about 0.17 g. of potassium cyanide. Experiments in which smaller quantities of cyanide were used to trace this factor will be discussed later.

THE ACTION OF PURE POTASSIUM CYANIDE ON PURE BENZALDEHYDE

It will be clear from the experiments mentioned above that pure potassium cyanide and pure benzaldehyde readily yield benzoin. As will be described later, the reaction is inhibited by impurities present in the potassium cyanide; this phenomenon explains the failure of Lachmann to obtain benzoin except in the presence of water or of benzoin itself.

Figure 1 shows the results of experiments on the rate of formation of benzoin at 100°C. The points and dotted curves refer to experimental results; the full curves have been calculated (see below).

An examination of the curves shows that: (a) The reaction is autocatalytic. (b) The initial rate of reaction depends on the quantity of potassium cyanide present. (c) Once normal reaction has begun the rate is almost independent of the quantity of potassium cyanide present; thus, when rapid reaction has set in, the slope of the curve for 0.2 g. of potassium cyanide is almost the same as that of the curve for 6.2 g. (1 mol. proportion of potassium cyanide). (d) The autocatalyzed stage of the reaction is succeeded by a period of deceleration most marked with the smaller quantities of potassium cyanide.

We are evidently dealing with two concurrent reactions. The presence of potassium cyanide is necessary to produce benzoin, because if benzoin and benzaldehyde are shaken together at 100°C. the quantity of benzoin does not increase. Once benzoin is formed a second reaction sets in, in which benzaldehyde, potassium cyanide, and benzoin together yield benzoin.

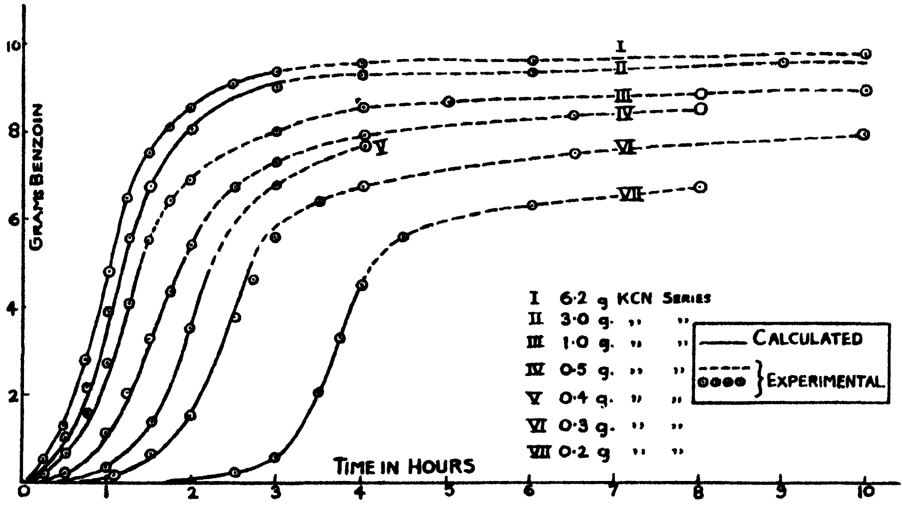

FIG. 1

Experiments in which 1 g. of benzaldehyde was replaced by 1 g. of benzoin showed that added benzoin behaves in the same manner as benzoin formed in the reaction.

THE QUANTITY OF POTASSIUM CYANIDE EFFECTIVE IN PRODUCING REACTION

Experiments at 100°C., some lasting up to 30 hours, with 10 g. of benzaldehyde and increasing quantities from 0.1 to 0.2 g. of potassium cyanide, benzoin being added to serve as a catalyst, showed that the formation of benzoin began only with 0.18 g. potassium cyanide.

Experiments were then made in which 20 g., 10 g., and 5 g. of benzaldehyde were shaken, respectively, with 1.0 g., 0.5 g., and 0.25 g. of potassium cyanide. The results are plotted in figure 2, the quantities obtained from

20 g. of benzaldehyde being halved and those with 5 g. being doubled. The three curves do not coincide but instead, as the quantity of cyanide decreases, the relative rate of reaction falls off.

On the same figure there are plotted the results of an experiment with 10 g. of benzaldehyde and 0.3 g. of potassium cyanide; the results correspond closely with the doubled quantities from 5 g. of benzaldehyde and 0.25 g. of potassium cyanide.

A study of figure 2 indicates that we can assume that 10 g. of benzaldehyde and about 0.33 g. of potassium cyanide yield twice as much benzoin in a given time as 5 g. of benzaldehyde and 0.25 g. of potassium cyanide. If then y is the quantity of potassium cyanide rendered inactive we have

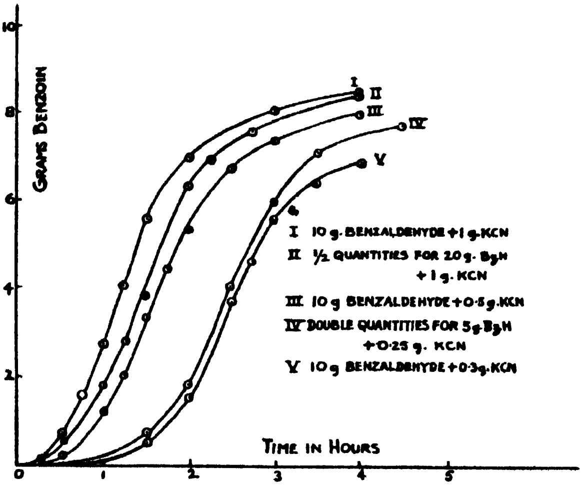

FIG. 2

$$0.33 - y = 2\,(0\;25 - y)$$

whence

$$y = 0.17$$

This is in agreement with the results of the direct determination.

In what follows we subtract 0.17 g. from the "gross" quantities of potassium cyanide used in each experiment to obtain "net" effective quantities.

The inhibiting factor

Having established the fact that in some way up to 0.17 g. of potassium cyanide was poisoned in each experiment, attempts were made to determine the cause of this.

In the preliminary experiments (p. 729) made in the early stages of the research, 1 g. of potassium cyanide was used. As figure 1 shows, with this quantity of cyanide the rate of reaction is not sensitive to small changes in the amount of cyanide, so that it became advisable to repeat such experiments with smaller quantities of cyanide (table 1).

Three factors might be responsible for the poisoning: (a) the glass of the bottle; (b) the rubber ring used to seal it; and (c) small quantities of oxygen enclosed in the bottle.

It will be seen from table 1 that if the rubber washer is removed, benzoin can be obtained from 0.15 g. of potassium cyanide. In the presence of 1 g. of rubber no benzoin is obtained from 0.15 g. of potassium cyanide. It is possible that the effect of rubber is due to the sulfur it contains for, as will be shown later (Part II), sulfur is a powerful anticatalyst for the reaction.

TABLE 1

EXPT. NO.	BENZALDEHYDE USED	KCN USED	TIME OF SHAKING AT 100°C	SPECIAL CONDITIONS	YIELD OF BENZOIN	CONCLUSION
	grams	*grams*	*hours*			
1	10	0 15	4	Sealed in an atmosphere of nitrogen	1 69	Oxygen of air or rubber appears to stop the reaction
2	10	0 15	4	Sealed in air	1 70	Oxygen does not stop the reaction
3	10	0 15	4	Sealed in air with rubber pieces (1 g. present)	Nil	Rubber stops the reaction
4	10	0 10	5	Sealed in air	0 2	
5	10	0 10	5	Sealed in an atmosphere of nitrogen	0.17	
6	10	0 05	5	Sealed in air	Nil	Residual inhibiting factor present
7	10	0.08	5	Sealed in an atmosphere of nitrogen	Nil	

Even with a reaction vessel sealed in an atmosphere of nitrogen, no benzoin is yielded by less than 0.10 g. of cyanide. The reason for this is still obscure.

THE ACCELERATED STAGE OF THE REACTION

In the mathematical formulation of these reactions in highly condensed systems, of the type in which a solvent itself is undergoing reaction, it has seemed to us preferable to use molecular concentrations (mole fractions) rather than volume concentrations. This is unusual, but may be justified by the following consideration: If in a reacting mixture of benzaldehyde and benzoin, one imagines a benzaldehyde molecule surrounded by a closely packed mixture of benzaldehyde and benzoin molecules, then the number of collisions it will make in a given time with surrounding benzoin molecules depends not so much on the total volume of the liquid, which will not vary greatly as benzaldehyde is converted into benzoin, but on the fraction of benzoin molecules among the surrounding molecules, that is, on the mole fraction.[2]

It is admitted that this consideration has only approximate validity, since the molecules of benzoin are larger than those of benzaldehyde, but it forms an approach to what is practically a new branch of chemical kinetics, in which there is little precedent to follow.

An examination of the curves obtained with small quantities of potassium cyanide when the autocatalytic[3] reaction is predominant indicates that the total rate of this reaction in a given system is independent of the quantity of potassium cyanide present (p. 729), but is proportional to the total amount of benzoin present, and to the square of the molecular fraction of benzaldehyde. This can be interpreted to mean that the rate of this homogeneous reaction is proportional to the number of collisions of molecules of benzoin each with two molecules of benzaldehyde (p. 737). We may write therefore,

$$\text{Total rate of homogeneous reaction in a given system} = K_1\,[C_6H_5CHO]^2\,\underline{C_6H_5COCHOHC_6H_5} \qquad (1)$$

where $C_6H_5COCHOHC_6H_5$ stands for the total amount of benzoin present in the system.

Since this reaction which is accelerated by benzoin requires the presence of potassium cyanide, but is not affected by the total quantity present, it would seem that it is the trace of potassium cyanide dissolved in benzaldehyde which induces the reaction.

The slower reaction involving the initial production of benzoin, is found by analysis of the reaction velocity curves to have, in a given system, a total rate proportional to the total quantity of potassium cyanide present, and to the square of the molecular concentration of benzaldehyde. Since potassium cyanide is practically insoluble in benzaldehyde at 100°C., it is evident that the proportionality factor for the quantity of potassium cyanide is in reality a factor for the total surface of potassium cyanide present, as this with uniform cyanide is proportional to the total quantity present. We may therefore (see p. 738) regard the reaction as heterogeneous, and as having a total rate proportional to the total surface of cyanide present, to the fraction of the surface covered, and to the rate at which benzaldehyde molecules collide with unit area of surface.

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[2] It is assumed that a given molecule is always surrounded by the same number of neighboring molecules.

[3] A discussion of the mathematical treatment of simple autocatalytic reactions (logistic equation) is given by Reed and Berkson (J. Phys. Chem. 33, 760 (1929)).

We have consequently,

$$\text{Total rate of heterogeneous reaction} = k[\mathrm{C_6H_5CHO}]^2\,\underline{\mathrm{KCN}}$$

where $\underline{\mathrm{KCN}}$ stands for the total amount of potassium cyanide present. For a given quantity of potassium cyanide in the system we may write,

$$\text{Total rate of heterogeneous reaction} = k_2[\mathrm{C_6H_5CHO}]^2 \qquad (2)$$

We may now proceed to write the differential equation for the concurrent reactions.

Let n be the number of moles of $\mathrm{C_6H_5CHO}$ remaining at time t, and $N =$ the number of moles of benzaldehyde initially taken. Then $\frac{N-n}{2} =$ the number of moles of benzoin present at time t, $\frac{N+n}{2} =$ total number of moles present, and molecular fraction of benzaldehyde $= \frac{2n}{N+n}$.

Then the total rate of reactions 1 and 2 is given by

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = k_1 \left(\frac{2n}{N+n}\right)^2 \left(\frac{N-n}{2}\right) + k_2 \left(\frac{2n}{N+n}\right)^2 \qquad (3)$$

so that,

$$-2k_1(t-c) = \frac{-N^2}{(N+X)n} + \frac{N(3N+2X)\ln n}{(N+X)^2} - \frac{(2N+X)^2 \ln (N+X-n)}{(N+X)^2} \qquad (4)$$

where $X = 2k_2/k_1$, and c is a constant.

For calculation purposes it is more convenient to express quantities in grams than in moles, and for a system containing initially 10 g. of benzaldehyde, equation 4 becomes, when x is small,

$$t - c' = -\frac{1}{k_1}\left[-\frac{5}{n'} + 3.45 \log n' - 4.60 \log (10 + X' - n')\right]$$

where c', n', X' refer to gram-units; k_1 is independent of the units in which the benzaldehyde is expressed.

For the experiments under consideration, $k_1 = 5.7$, and k_2' for 1 g. of effective potassium cyanide per 10 g. of benzaldehyde $= 0.185$. Hence we have the values given in table 2.

The equations to be employed for (a) 0.2 g. of potassium cyanide and for (b) 6.2 g. of potassium cyanide for 10 g. of benzaldehyde are, respectively,

$$\text{(a)} \quad -5.7(t - 3.70) = \frac{-5}{n'} + 3.45 \log n' - 4.60 \log (10.002 - n')$$

$$\text{(b)} \quad -5.7(t - 0.75) = \frac{-4.8}{n'} + 3.3 \log n' - 4.4 \log (10.4 - n')$$

Equations for other quantities of potassium cyanide are obtained in a similar manner.

The application of these equations to calculate the course of the time reaction curve for the accelerated stage is shown in figure 1. During the accelerated stage of the reaction the experimental and calculated results are in satisfactory agreement. It should be stated that the homogeneous catalyzed reaction is much the faster of the two reactions involved.

THE LATER STAGES OF THE REACTION

The rapid decrease in the rate of reaction when about half of the benzaldehyde present has been converted is a striking feature of the experimental curves.

TABLE 2

KCN USED (a)	KCN EFFECTIVE $(b = a - 0.17)$	$k_2' = 0.185b$	$X' = \frac{2k_2'}{k_1} = \frac{2k_2'}{5.7}$
grams	*grams*		
0.2	0.03	0.006	0.002
0.3	0.13	0.024	0.01
0.33*	0.16	0.030	0.011
0.4	0.23	0.043	0.015
0.5	0.33	0.061	0.02
0.59†	0.42	0.08	0.030
1.0	0.83	0.15	0.05
3.0	2.83	0.53	0.20
6.2	6.03	1.12	0.40

* Double quantities for 5 g. of C_6H_5CHO + 0.25 g. gross KCN.

† Half quantities for 20 g. of C_6H_5CHO + 1 g. gross KCN.

This consideration led to the determination of the solubility of benzoin in benzaldehyde at 100°C.; 10 g. of benzaldehyde at 100°C. dissolve 10.4 g. of benzoin, so that when about 50 per cent of the benzaldehyde has been converted, saturation of the remaining aldehyde with benzoin occurs, and any further formation of benzoin involves precipitation of this substance. This consideration, while it explains a falling-off in the rate of reaction, does not show why this decrease is more rapid with the smaller quantities of potassium cyanide.

This phenomenon can be explained by assuming that the precipitated benzoin adsorbs dissolved cyanide from the solution. With a small quantity of cyanide a small quantity of benzoin will remove all from solution; with a large quantity of cyanide a large quantity of benzoin must be precipitated before all the cyanide is removed. We expect, therefore, that with a large quantity of cyanide the fall in the rate of reaction will be due for the most part to a contraction in the amount of saturated solution and not to the stoppage of the homogeneous reaction. We can, accordingly, calculate the rate of reaction as follows:

Let B = number of moles of benzoin soluble in 1 mole of benzaldehyde at 100°C. If the solution first becomes saturated when m moles of benzaldehyde remain, we have then $\left(\frac{N - m}{2}\right)$ moles of benzoin, and hence

$$Bm = \frac{N - m}{2}$$

and

$$m = \frac{N}{2B + 1}$$

The total rate of reaction when the solution becomes saturated is (see equation 3)

$$-\frac{dm}{dt} = k_1 \left(\frac{2m}{N + m}\right)^2 \left(\frac{N - m}{2}\right) + k_2\left(\frac{2m}{N + m}\right)^2 = \frac{k_1}{(B + 1)^2} \left(\frac{BN}{2B + 1} + \frac{X}{2}\right)$$

If now for convenience in calculation we work in grams and put B' = number of grams of benzoin soluble in 1 g. of benzaldehyde at 100°C., and assume that the solution first becomes saturated when m' grams of benzaldehyde remain, we have

$$\frac{B'}{2} = B$$

and

$$\frac{-dm'}{dt} = \frac{2k_1}{(B' + 2)^2} \left(\frac{B'N'}{B' + 1} + X'\right)$$

Putting $k_1 = 5.7$, $N' = 10$, $X' = 0.4$,[4] and $B' = 1$, we have

$$\frac{-dm'}{dt} = \frac{11.4}{9} (5 + 0.4)$$

As a first approximation, we can neglect the heterogeneous reaction with potassium cyanide and write

$$-\frac{dm'}{dt} = \frac{11.4 \times 5}{9} = 6.4$$

Since it is a uniform saturated solution of benzoin in benzaldehyde which is undergoing reaction we have,

$$-\frac{dn'}{dt} = -\frac{n'}{m'} \times -\frac{dm'}{dt} = \frac{6.4n'}{m'}$$

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[4] This corresponds to 6.2 g. of potassium cyanide (table 2).

And since $m' = 5$,

$$-\frac{dn'}{dt} = 1.28n'$$

whence,

$$-t + c = 0.78 \ln n' = 1.80 \log n'$$

When $t = 1, n' = 5$, so we have

$$-t + 2.26 = 1.80 \log n'$$

The application of this equation to calculate the course of the reaction velocity curve for 6.2 g. of potassium cyanide from 5 g. of benzoin onwards is shown by curve 1 in figure 1. The agreement is satisfactory. When the quantity of benzoin formed is large, the homogeneous reaction is affected by removal of potassium cyanide and the actual rate decreases more rapidly than the calculated rate.

The agreement with the calculated equation for 3 g. of potassium cyanide is also found satisfactory (see figure 1, curve 2, from 5 g. of benzoin onwards).

With smaller quantities of potassium cyanide, i.e., quantities less than 3.0 g., the dissolved cyanide is removed too rapidly to enable the above equations to apply.

EXPERIMENTS WITH POTASSIUM CYANIDE AND BENZALDEHYDE AT 30°C.

Curves in figure 3 show the results of some experiments at 30°C. They are of interest as showing that pure benzaldehyde and pure potassium cyanide can yield benzoin at room temperature.

THE MECHANISM OF THE HOMOGENEOUS BENZOIN REACTION IN THE ABSENCE OF WATER

The experimental results show that the total rate of this reaction is proportional to

$$[C_6H_5CHO]^2\underline{C_6H_5CHOHCOC_6H_5}$$

molecular fractions being used in place of concentrations. If the reaction involved is of the type

$$C_6H_5CH(OK)(CN) + C_6H_5CHO + C_6H_5CHOHCOC_6H_5 \rightarrow$$
$$C_6H_5C(OK)(CN)CHOHC_6H_5 + C_6H_5CHOHCOC_6H_5$$

then if, as is likely, the concentration of $C_6H_5CH(OK)CN$, that is, of dissolved potassium cyanide, is proportional to the concentration of benzaldehyde, we can write the rate of reaction as proportional to

$$[C_6H_5CHO]^2\underline{C_6H_5CHOHCOC_6H_5}$$

The mechanism necessary to explain these kinetic results is essentially the same as that suggested by Lapworth (6).

While the un-ionized form of the cyanohydrin compound has been written, it may be that even in benzaldehyde solution the trace present is always ionized. On the other hand, as regards the mobility of the hydrogen atom in the cyanohydrin compound, it would not appear to be important whether it is or is not ionized.

The necessity for the presence of benzoin before the homogeneous reaction can proceed is not easy to explain.

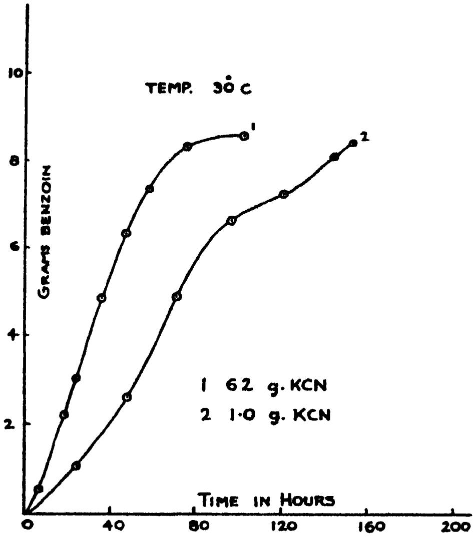

FIG. 3

THE MECHANISM OF THE HETEROGENEOUS BENZOIN REACTION IN THE ABSENCE OF WATER

This reaction obviously takes place at the surface of the undissolved potassium cyanide. The total rate of formation of benzoin in this reaction may be regarded as proportional to the number of collisions of benzaldehyde molecules on that portion of the potassium cyanide surface which is covered by similar molecules. If the adsorption is small, then the fraction of the surface covered by the benzaldehyde molecules will be proportional to the concentration of benzaldehyde in the liquid phase (3), the number of collisions on the whole surface is also proportional to the benzaldehyde concentration, while the area of the whole surface varies with the amount of potassium cyanide present. Accordingly the rate of formation of benzoin under these conditions is proportional to

$$[C_6H_5CHO]^2\underline{KCN}$$

which is the equation deduced from the kinetic data (p. 734).

The mechanism of this reaction is much the same as that postulated for the homogeneous reaction. We assume that the adsorbed benzaldehyde is present as the cyanohydrin compound, and that when collision occurs, condensation to the benzoin cyanohydrin compound takes place. This then eliminates benzoin. In the formation of the cyanohydrin compounds the potassium and cyanogen ions may remain partly attached to the potassium cyanide lattice, reverting to it when eliminated from the potassium cyanide compound.

SUMMARY

1. It is shown that pure potassium cyanide and pure benzaldehyde react in absence of water to give benzoin.
2. Two concurrent reactions take place—a fast homogeneous autocatalytic reaction and a slow heterogeneous reaction.
3. The results have been treated mathematically on this basis.
4. The mechanisms of the reactions in the absence of water have been discussed.

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NEW BOOKS

Line Coördinate ·Charts for Vapor Pressure–Temperature Data. By FRANK E. E. GERMANN and ODIN S. KNIGHT. 2 charts, 22.9 x 61 cm. University of Colorado, Boulder, Colorado. Price: $2.00.

One of the great obstacles in physical, organic, and industrial laboratories has been the lack of at least approximate vapor pressure–temperature data. The authors have supplied this need by the production of a line coordinate chart based on the integrated form of the Clausius-Clapeyron equation. The reciprocals of the absolute temperatures have been plotted against the logarithms of the vapor pressures over the range of 500 to 900 mm. The vapor pressures obtained by various authors have been studied, and weighted curves drawn. In all cases the individual variations among the results for a given compound are greater than the possible error made in assuming the lines to be straight.

The 183 compounds given are conveniently separated into chain and ring compounds. Each class is provided with two scales: chain compounds, 0° to 125°C. and 105° to 230°C.; ring compounds, 65° to 225°C. and 185° to 390°C. The use of these charts makes calculations for corrections in boiling points due to variation in pressure unnecessary. The charts permit temperature readings within 0.25°C. if the pressure is known, or pressures within 2 mm. if the temperature is known. A knowledge of the prevailing barometer pressure only is required.

Ample directions are given for the interpolation of boiling point or of vapor pressure values, and for the insertion of new data as it may appear. These charts will meet a long-felt want in all laboratories, whether at sea-level or at higher altitudes.

J. N. PEARCE.

The Solid Products of the Carbonization of Coal. Chemical Department, South Metropolitan Gas Co. Paper cover; 123 pp.; 41 figures; 45 tables. London: South Metropolitan Gas Co., 709 Old Kent Road, S.E. 15, 1934.

This monograph gives the results of an original investigation conducted by the chemical staff of the South Metropolitan Gas Co. over a period of several years in an endeavor to increase the use of coke as a domestic fuel. Following a short introduction, Chapter II, on an investigation into the possibility of producing by the carbonization of coal a smokeless solid fuel suitable for the domestic grate fire, describes test methods for determining the ignition temperature, combustibility, reactivity to carbon dioxide, steam, and sulfuric acid, and electrical conductivity of cokes and chars. Application of these tests to a series of cokes made at increasingly higher carbonizing temperatures, ranging from 500 to 1050°C., showed that reactivity to air, carbon dioxide, steam, and sulfuric acid decreased and electrical conductivity increased with increasing temperature of carbonization. These changes in coke characteristics were most marked at about 700°C. carbonization temperature and coincided with the change in appearance from a dull black to the characteristic silvery sheen of high temperature coke. The absorptive capacity of the cokes for carbon dioxide increased sharply with increasing temperature of carbonization up to a maximum at 700°C., and then fell rapidly. Deposition of graphitic carbon reduced slightly the reactivity of the high temperature cokes but seemingly was not the major cause of the large difference between low and high temperature cokes. Alteration of the physical structure produced by any modification of the high temperature carbonizing process likely to be practicable was quite ineffective in producing a substantial improvement in the combustibility of the coke.

As a result of this investigation the authors believe that the difference in reactivity between low and high temperature coke is due to a profound change in chemical rather than physical structure. Assuming that the benzene ring nucleus plays an important part in the chemical structure of coal, they believe that in the low temperature carbonization of coal, i.e., below 700°C., side chains are stripped from the nucleus without coalescence of these nuclei; whereas, in carbonization above 700°C., the single nuclei coalesce to form complex polycyclic compounds coincident with a marked evolution of hydrogen. The closer association of the carbon atoms without the frequent interposition of hydrogen atoms suggests a plausible explanation of the reduced chemical activity.

Chapter III states the characteristics of a satisfactory low temperature fuel as having a size between 1 and 2 inches, low ash, not over 5 per cent moisture, about 13 per cent volatile matter, and an electrical resistivity of not less than one million ohms. In order that the coke may be readily ignitable and freely burning in the ordinary domestic grate the coal must be carbonized below 700°C.

Chapter IV, on the use of high temperature coke as a domestic fuel, describes the "metro" coke grate which was developed for use of high temperature gas cokes. Burning tests and the effect of residual volatile matter, size, ash, and volume of ash on the performance in grates and domestic hot water boilers are given. Optimum characteristics are size 1 to 2 inches, moisture 3 per cent, volatile therms per ton $2\frac{1}{2}$, and as low ash volume as possible.

Although high combustibility is not of the same importance in American practice because coke is used in central heating furnaces rather than open grates, yet American fuel technologists will find this monograph worthy of careful study. Physical chemists will be interested in the theory advanced in explaining the reduction of reactivity with increasing temperature of carbonization.

A. C. Fieldner.

THE ELECTROKINETIC POTENTIAL AND THE STABILITY OF COLLOIDS[1]

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Received June 14, 1934

Experimental evidence (6) shows that the stability of hydrophobic colloids is determined by the electrokinetic potential of the particles. In the case of hydrophilic colloids, however, the experiments indicate (1,4) that coagulation depends primarily on the amount of hydration, while the ζ-potential seems to be of much less importance. The question arises, therefore, whether the electric forces are sufficient to explain the stability of hydrophobic colloids. This problem has been investigated by A. March (3). He finds that the observed electrokinetic potentials are at least ten times too small to account for the existence of colloids with microscopic particles. March comes to the conclusion that the stability of colloids is essentially due to the existence of a protecting skin around every particle. This result is in agreement with the fact that colloidal particles do not grow or flow together during coagulation. Even liquid particles remain separated after coagulation. In view of the experimental facts, it seems natural to assume that in the case of hydrophilic colloids this protecting skin is formed by the hydrated water molecules.

For hydrophobic colloids this explanation can obviously only be accepted if we can understand the origin and nature of this protecting skin. We must prove that the energy necessary to destroy this skin is larger than the energy of the temperature motion of the partices. Finally its existence must be closely connected with the electrokinetic potential in such a way that its influence vanishes with small ζ-potentials.

In a recent paper (5) I have proposed the following explanation of the origin of this protecting skin: The electric double layer creates a very strong inhomogeneous electric field around each particle. This field produces by electrostriction a large hydrostatic pressure in the range of the double layer. We find, therefore, around each particle a thin shell where the water is under considerable pressure. It is this shell which acts as the protecting skin. According to this theory the mechanism which produces the stability of colloids is very similar for hydrophilic and hydrophobic sols. The difference lies in the fact that in hydrophilic colloids the water molecules are "attached" to the surface of the micelle by chemical (adsorption) forces and hence coagulation is to a large degree independent of the ζ-potential. In hydrophobic colloids the water molecules are only "attracted" to the surface by the electrostatic forces of the double layer, and hence their stabilizing influence diminishes as the ζ-potential gets smaller.

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[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14-16, 1934.

The energy of this electrostatic effect can be calculated by means of the same considerations as given by Zwicky (7) for the electric field around ions. We consider a plane diffuse double layer. If the ζ-potential is not larger than 50 millivolts the electric potential φ at a distance x from the surface of the particle is given by

$$\varphi = \zeta e^{-Kx}$$

where $\frac{1}{K} = \lambda$ is the effective thickness of the double layer. The electric field at the distance x is

$$E = \mathrm{K}\zeta e^{-Kx}$$

and the dielectric polarization

$$P = \frac{D-1}{4\pi} E$$

where D is the dielectric constant of water. We use the value $D = 80$. Dielectric saturation effects can be neglected. According to A. H. Lorentz and Dällenbach (2) the force exerted on 1 cc. of the dielectric is then

$$F = \frac{1}{4\pi}\left[1 + \frac{(D-1)(3D+7)}{5}\right] E \frac{\mathrm{d}E}{\mathrm{d}x}$$

and hence the hydrostatic pressure p at the distance x from the surface

$$p = \int_x^\infty F\,\mathrm{d}x = 155\,\zeta^2 K^2 e^{-2Kx}$$

The maximum pressure exists along the surface $x = 0$ and reaches the value

$$p_0 = 17K^2\zeta^2\,10^{-10} \text{ kg. per cm.}^2$$

In this formula ζ is the value of the potential in volts and has usually values smaller than 0.1. For a monovalent electrolyte K^2 has, according to Debye and Hückel, the value

$$K^2 = \gamma\cdot 1.07 \times 10^{15}$$

where γ is the molar concentration of the electrolyte. Using $\zeta = 0.1$, $\gamma = 1/1000$ we get therefore a maximum pressure of about 18 atmospheres.

Five to ten times larger values of this pressure can be calculated if we take into account the curvature of the surface of small colloidal particles. In the case of a spherical particle the potential decrease is given by

$$\varphi = A \frac{e^{-Kr}}{r}$$

and since the pressure depends on $E = -\frac{\partial \varphi}{\partial r}$ and $\frac{\partial E}{\partial r} = -\frac{\partial^2 \varphi}{\partial r^2}$ one realizes that this more rapidly decreasing potential gives rise to a larger pressure.[2]

It is intended to show here only that the proposed theory gives results of the correct order of magnitude. We shall, therefore, consider only the case of the plane double layer, keeping in mind, however, that for colloids the numerical values of all results will usually be considerably larger.

This hydrostatic pressure will result in a volume contraction of the colloid and leads to the conclusion that agglutination produces an increase of the volume. This increase is given by

$$\Delta V = 4\pi N \int_r^\infty \kappa p(r) r^2 \, dr$$

where $\kappa = 45 \cdot 10^{-6}$ is the compressibility of water and N the number of colloidal particles in one liter. The calculation gives, with the most favorable assumptions, an increase of 10^{-3} to 10^{-4} cc. for one liter of colloid. Linder and Picton (8) observed an expansion of this order of magnitude for a sol of ferric hydroxide.

While the work of compression $\int p dV$ is small and can be neglected, Zwicky has pointed out that this electrostrictive effect produces an appreciable change of the free energy of the water. According to measurements of Bridgman the specific heat of water at room temperature decreases under the influence of pressure, and the free energy diminishes likewise. For small pressures the energy decrease is nearly linear and has the approximate value

$$\Delta U = 1.34 \cdot 10^{-3} \text{ cal. per gram} = 5.6 \cdot 10^4 \text{ ergs per gram}$$

for a pressure of 1 kg. per cm^2.

The layer of compressed water on the surface of a colloidal particle is therefore the seat of a negative free energy. The amount of energy necessary to destroy 1 cm.^{2} of this film is given by

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[2] The calculation of this case has been carried out, but since the result cannot be given in analytical form, it will not be given here. The above expressions for φ are only valid for small values of ζ. The solution for large values of ζ leads to even larger values of $\frac{d\varphi}{dr}$ and hence to still larger pressures.

$$U = \int_0^\infty 5.6 \cdot 10^4 p \, dx = 4.8 \cdot 10^{-5} K\zeta^2 \text{ ergs per cm.}^2$$

Introducing again $\zeta = 0.1$, $\gamma = 1/1000$ gives

$$U = 0.5 \text{ erg per cm.}^2$$

If we use the accurate solution for the plane double layer (5) for a Z-Z valent electrolyte the expression for U is

$$U = 4.8 \cdot 10^{-5} K z \zeta^2 \left(\frac{\sinh \psi}{\psi}\right)^2$$

where

$$\psi = \frac{ze}{4kT}\zeta$$

k = Boltzmann's constant, and e = electronic charge. This gives for $Z = 3$, $\gamma = 1/1000$, and $\zeta = 0.1$

$$U = 3 \text{ ergs per cm.}^2$$

Taking into account the curvature of the surface we can expect values of 10 ergs per cm^2. This is almost of the same order of magnitude as the surface tensions of liquid–liquid interfaces, and we can readily understand that this surface layer of compressed water is able to stabilize the colloid.

If we assume that coagulation can occur only if this surface layer is destroyed in the area of contact, and if we assume that for large particles this area of contact is larger than 10^{-14} cm.^{2}, we see that the temperature motion of the particles is not large enough to destroy the protecting skin. Hence, the colloid is stable. A small reduction of the ζ-potential decreases the energy necessary to produce coagulation, and since U is proportional to ζ^2 the stability of a colloid is very sensitive to small changes of the electrokinetic potential.

Making allowance for the approximations used, the proposed theory is therefore able to explain the dependence of the stability of hydrophobic colloids on the electrokinetic potential.

It is interesting to note that the theory leads to the conclusion that the degree of stability of hydrophobic colloids should decrease rapidly for temperatures above 80°C. Bridgman's measurements show that above 80°C. the free energy of water decreases only slightly with pressure. For pressures larger than 1000 kg. per cm.^{2} the energy increases at this temperature. It seems possible that the coagulation produced by heating of certain hydrophobic colloids (Pt) is a consequence of this effect.

The electrostrictive effect will also reduce the specific heat of colloids. This effect can be calculated with the method given by Zwicky (7) for electrolytes, but owing to the small number of colloidal particles this effect is too small to be measured.

The magnitude of the electrostrictive effect depends on the type of electric double layer, but it will exist even for a Helmholtz double layer.

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THE INFLUENCE OF SALTS ON THE POTENTIAL AND CHARGE OF INERT AND PROTEIN SURFACES[1]

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INTRODUCTION

At a previous Symposium (1) I have had the pleasure of reviewing the theory and experiments pertaining to the influence of size, shape, and conductance of microscopically visible particles on their electric mobilities. Since that time publications by Mooney (14), by Henry (13), and by Bikerman (10) have given further information which has increased our perception of the difficulties involved in correlating theory with experiment and which is suggestive of further experimentation. At this Symposium rather than review these advances it seems desirable to consider certain other developments in the treatment of the ζ-potential and the net charge density, σ, of the surfaces of large particles. If large particles in simple salt solutions are considered, much of the difficulty met in applying the theory of electrokinetics to small particles is avoided. It has been found that if the effects of ***salts not reversing the sign of surface charge*** are investigated in the light of modern electrolytic theory, certain simplifications result. These simplifications have consisted of a study of surfaces the charges of which depend primarily upon: (1) adsorption of ions (quartz, graphite, etc.); (2) ionization (amorphous proteins).

Although the complex arrangements existing at cell surfaces have, as yet, prevented our obtaining a picture suitable for all cells, in certain instances, the study of biological materials like blood cells, bacteria, and immune substances indicates that surfaces with properties somewhat similar to these two limiting types may be encountered (2). With the glimpses of possible arrangements obtained by means of the simpler chemical models to be presented here, it is hoped that an appreciation of the simpler models will justify our dissatisfaction with mere glimpses, and that further study of these models in connection with experiments on the biological materials themselves will enable us to find the constitution and properties of cell surfaces more comprehensible.

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[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

IONS

If the concentration of an aqueous solution of, say, potassium chloride is increased, the electric mobilities of the ions, K^+ and Cl^-, decrease. This typical decrease in the ionic electric mobility, v, is depicted in figure 1, where the change in v_{K^+} with the molar concentration, c, of potassium chloride is given. Note that the value of v_{K^+} is greatest at infinite dilution, and that the decrease in v_{K^+} can be approximately described by the equations of the Debye-Onsager theory. The case of ionic electric mobility of this type represents the limiting case of a very small particle, the charge of which remains constant while the electric mobility changes.

"INERT" SURFACES

In the cases of inert and of protein surfaces, and also, of biological systems, the problem becomes more general in nature, for we must deal with particles having diameters from the order of 1×10^{-7} cm. to those of the order of macroscopically visible particles including flat surfaces. The effects of salts on the electric mobility of microscopic and ultramicroscopic particles can be readily studied by the method of electrophoresis; or, analogously, streaming potentials and electroösmotic mobilities can be measured in tubes and diaphragms. These measurements lead to the calculation of the electrokinetic potential, ζ, by means of the equations for large particles (13, 14):

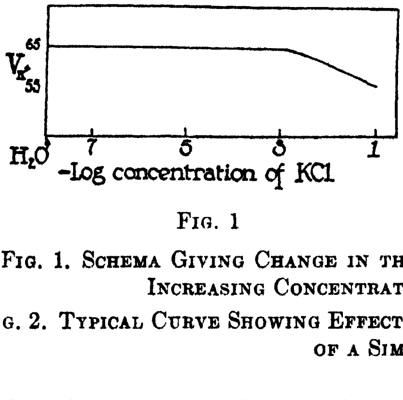

FIG. 1

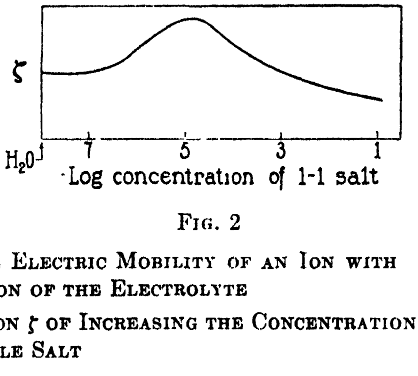

FIG. 2

FIG. 1. SCHEMA GIVING CHANGE IN THE ELECTRIC MOBILITY OF AN ION WITH INCREASING CONCENTRATION OF THE ELECTROLYTE

FIG. 2. TYPICAL CURVE SHOWING EFFECT ON ζ OF INCREASING THE CONCENTRATION OF A SIMPLE SALT

$$\zeta_E = \frac{4\pi\eta v}{D} \tag{1a}$$

$$\zeta_S = \frac{4\pi\eta}{D}\,\frac{E}{PR} \tag{1b}$$

$$\zeta_O = \frac{4\pi\eta u}{D} \tag{1c}$$

Here ζ_E, ζ_S, and ζ_O refer to values of the electrokinetic potential calculated from measurements of v, the electric mobility, of E, the streaming potential, and of u, the electroösmotic mobility, respectively; η is the coefficient of viscosity and D the dielectric constant of the medium; P is the pressure, and R is the specific resistance of the liquid in the tube or diaphragm. All units are C.G.S. electrostatic. For reasons stated elsewhere it is reasonable to assume that the values of D and η in the electric double layer approximate those in the bulk. When the radius of the particle is not large compared with the effective thickness of the electric double layer, the constant 4π in equations 1a to 1c must be modified (13, 14).

For the past two decades, quantitative measurements of the effect of salts on v, $\frac{E}{PR}$, and u have been studied on "inert" surfaces like glass, quartz, paraffin oil, collodion, cellulose, and graphite.[2] If we restrict our present discussion to salts not reversing the sign of surface charge, and calculate ζ by means of equations 1a to 1c as the mode of experimentation may determine, the shape of the ζ–c curve is usually that given by figure 2. This typical ζ–c curve on comparison with the v–c curve in figure 1 differs markedly from the typical v–c curve for ions. On the addition of salt, a maximum in the ζ–c curve (figure 2) is observed (3), usually at concentrations of the order $1 \times 10^{-5}\,M$. The ζ-potential $\left(\text{or } v, u, \text{and } \frac{E}{PR}\right)$ then decreases in much the same way that simple ionic mobility decreases. How can we explain this curious type of curve? Theoretical consideration of this problem by Gouy (11), Stern (16), and Gyemant (12) indicated that the charging process of the surface must be considered. The charge of the simple ion K^+, as has been mentioned, remains constant as v_{K^+} decreases. This is by no means the case with "inert" surfaces. The net surface charge density, σ, changes as more ions are added to the solution (5, 6, 14, 15). In general, for an infinite plane surface, σ can be calculated by combining the Poisson and Boltzmann equations. The integrated equation for σ is, in systems consisting essentially of two ions,

$$\sigma = \sqrt{\frac{\mathbf{N}D\mathbf{k}T}{2\pi \times 1000}\, c_{1[2]}\, z_{1[2]} \left[\frac{1}{z_2}\left(e^{+z_2 \frac{\mathbf{e}\zeta}{\mathbf{k}T}} - 1\right) + \frac{1}{z_1}\left(e^{-z_1 \frac{\mathbf{e}\zeta}{\mathbf{k}T}} - 1\right)\right]} \quad (3)$$

where $\mathbf{N}$ is Avogadro's number, $\mathbf{k}$ Boltzmann's constant, c the molar concentration, e the base of the natural logarithm, $\mathbf{e}$ the electronic charge, z the valence, and T the absolute temperature. In case $Z_1 = -Z_2 = Z_3$ in aqueous media, equation 3 reduces to

$$\sigma = 2\sqrt{\frac{\mathbf{N}D\mathbf{k}T}{2\pi \times 1000}}\, \sqrt{c}\, \sin h\, z\, \frac{\mathbf{e}\zeta}{\mathbf{k}T}$$

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[2] References to these publications may be found in the citation, Abramson and Mueller, or in detail in Chapters VI, VII, and VIII of the writer's monograph (2).

or

$$\sigma = 2\alpha\sqrt{c}\sin h\frac{z\zeta}{2\beta} \tag{3a}$$

where $\alpha = 17,650$ and $\beta = 0.025$ volt at 18°C. Equations 3 and 3a give us a means of following changes in the net surface charge as the number of ions in the solution increases.

Keeping in mind the complex form of the ζ–c curve (figure 2), examine the σ–c curves (figures 3 to 8). It is important to bear in mind that values of σ given in these curves have been corrected for the original charge due to the ions in distilled water (7). In each case the total charge, σ_T, has first been calculated. This total charge is due both to the ions of the solvent and dissolved carbonic acid and to the ions of the added salt. If σ_W is that due to the ions of the solvent and carbonic acid alone, the charge due to the salt is evidently

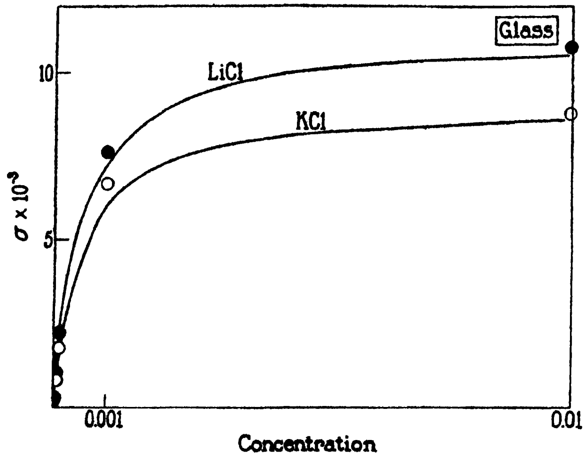

FIG. 3. THE EFFECT OF SALTS ON THE SURFACE DENSITY OF NET CHARGE ON GLASS

The points have been calculated by means of equation 3 from data of Furutani, Kurokochi, and Asoda. The smooth curves have been drawn according to the form of the Langmuir isotherm similar to equation 4.

$$\sigma_T - \sigma_W = \sigma$$

In every example calculated from the data in the literature (5, 6) for surfaces of glass, paraffin oil, silica gel, collodion, graphite, and cellulose, irrespective of the nature of the material and irrespective of differences in the salts themselves, the type of curve obtained is the same. In each instance σ increases sharply and almost linearly at low concentrations with the charge density apparently reaching a limiting value at about $c =$

0.001*M*. The descending part of the ζ–c curve given in figure 2 has frequently been taken to represent a "discharge" of the surface or of particles, since aggregation frequently occurs in this concentration range.

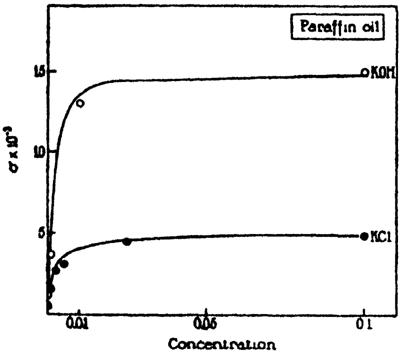

FIG. 4

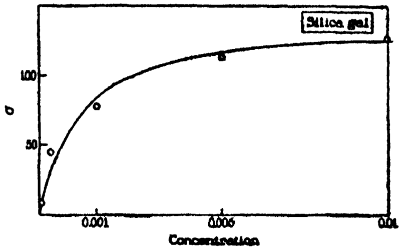

FIG. 5

FIG. 4. THE POINTS ON THE σ–c CURVE HAVE BEEN CALCULATED FROM DATA OF ELLIS PUBLISHED IN 1911, AND FROM DATA OF MOONEY (1931)

The smooth curves have been calculated by means of equation 4

FIG. 5. THE EFFECT OF A SIMPLE SALT ON SILICA GEL CALCULATED FROM DATA OF GLIXELLI AND WIERTELAK

The smooth curves are typical isotherms

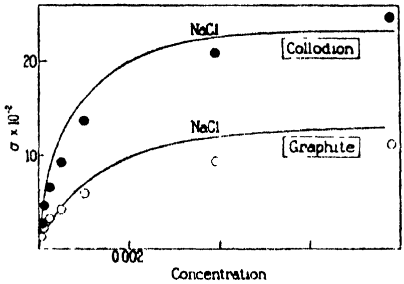

FIG. 6

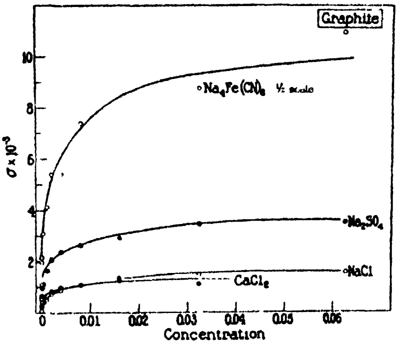

FIG. 7

FIG. 6. SIMILAR TO THE PRECEDING THREE FIGURES AND CALCULATED FROM DATA OF LOEB

FIG. 7. THE EFFECT OF SALTS NOT REVERSING THE SIGN OF CHARGE CALCULATED BY MEANS OF EQUATION 6a FROM DATA OF LOEB

Figures 3 to 8 demonstrate that, contrary to this notion, the addition of salt may actually be accompanied by an increase of the net charge even in the region of rapid coagulation. The complicated course of the ζ–c curve is due to the fact that ζ depends upon two variables, σ and κ (the "reciprocal thickness" of the diffuse ionic atmosphere), both of which depend on c.[8] We have here done what is tantamount to assuming the validity of the theory of the diffuse double layer to obtain the dependence of κ on c, permitting the calculation of σ (c).

σ and ζ presumably vary quite differently with c. As c increases $1/\kappa$ decreases. When c is small the increase in σ is more important, but as c increases the decrease in $1/\kappa$ becomes more important, flattening out the σ–c curve.

The reader will have noted that the form of all the σ–c curves bears a strong resemblance to the simple Langmuir adsorption isotherm. The smooth curves of figures 3, 4, 5 and 6 have actually been plotted by an equation of this form,

$$\sigma = \sigma_M \frac{\mathrm{B}c}{1 + \mathrm{B}c} \tag{4}$$

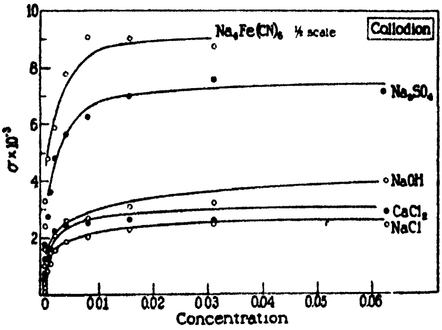

FIG. 8. SIMILAR TO FIGURE 7, CALCULATED FROM DATA OF LOEB

where $\sigma_M\mathrm{B}$ is the initial slope of the σ–c curve and σ_M is equal to the limiting value of σ within the concentration range. The agreement is excellent and indicates that selective adsorption of the negative ion takes place. The curves for the different alkali halogens and alkaline earth halogens show fewer variations than the curves for potassium bromide, iodide, and chloride. Especially large values of the charge are reached for the sulfates and ferrocyanides. The data indicate that for glass, graphite, and

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[8] The value of κ is

$$\kappa = \sqrt{\frac{4\pi \mathrm{N}e^2}{1000\,Dk T}}\,\sqrt{\Sigma c_i z_i^2}$$

where N is Avogadro's number, e the electronic charge, k Boltzmann's constant, c the concentration in moles per liter, and z the valence. The quantity $\Sigma c_i z_i^2$ is equal to twice the ionic strength, μ, of Lewis.

collodion, the adsorption potential increases in the series

$Cl^-, Br^-, I^-;$
$Li^+, Na^+, K^+, Rb^+, Cs^+;$
$Mg^{++}, Ba^{++}, Ca^{++};$
$I^-, (SO_4)^=, [Fe(CN)_6]^{\equiv}$

and that in general for these surfaces the adsorption potentials of the positive ions are considerably smaller than those of the negative ions.

The initial slope of the σ–c curves leads to values of the adsorption potentials of the same order of magnitude as found for the adsorption of gases.

It is of interest to calculate (neglecting the adsorption of positive ions) the fraction of the area occupied by ions in connection with the limiting value of σ. To take the case of glass, $\sigma_M = 9000$ E.S.U., representing about 2×10^{13} ions per cm.² If the area occupied by each ion is taken as 5×10^{-16} cm.², the limiting area occupied by the free negative is 0.01 cm.² or 1 per cent of the surface. This is a rather higher value than that deduced by previous investigators, but is compatible with the type of adsorption postulated by Langmuir's simple theory of adsorption.

In a future communication we shall give results of calculations by means of equation 3 for the σ–c curve for non-symmetrical cases of polyvalent ions not reversing the sign of charge. Using the Debye approximation for surfaces where $\frac{e\zeta}{kT}$ is relatively small, we have obtained preliminary indications that the form of the curve is exactly the same as that obtained by the rigorous expression (equation 3) for uni-univalent salts. Some of the curves obtained by the approximate formula are given in figures 7 and 8 (graphite and collodion). Compare these curves with the σ–c curves for the same substances using the full equation. There is obviously no difference in the shape of the curves.

PROTEINS

The study of the effect of salts on the charge of protein surfaces is simplified by the fact that the net charge of protein molecules dissolved in simple mineral acids can be determined by a thermodynamic method. Thus in a protein–HCl solution, we have, for example,

$$(Cl^-)_{Pr} = (Cl^-)_{Total} - \frac{a_{Cl^-}}{\gamma_{Cl^-}}$$

where the subscript Pr refers to the ions bound by the protein, the parentheses represent concentrations, and a and γ are activity and activity coefficient, respectively. If n is the time average of the net charge of the protein molecule, the expression,

$$n = (\mathrm{H}^+)_{\mathrm{Pr}} - (\mathrm{Cl}^-)_{\mathrm{Pr}}$$

gives a simple means of determining the net charge. Evidently the net charge of proteins having known molecular weights can be very closely determined from suitable electrometric measurements by making certain assumptions in regard to the activity coefficients of the ions present in the solution.

It has been found that the changes in charge as determined by thermodynamic methods agree with the changes in charge calculated by means of the Debye approximation (8). That is, in solutions of the same ionic strength the electric mobility of the same protein at different hydrogen-ion activities is directly proportional to the number of hydrogen (hydroxyl) ions bound. The theoretical expression predicting this relationship is to be found in the Debye-Henry approximation for the potential at the surface, where, for particles the size of protein ions,

$$v = \frac{1}{6\pi}\frac{\zeta_E D}{\eta}, \qquad (\kappa r > 30) \tag{5}$$

and

$$\zeta = \frac{Q}{Dr}\frac{1}{(1 + \kappa r)} \tag{6}$$

and

$$Q = 4\pi r^2 \sigma \tag{6a}$$

Consider in the light of these equations the special case of a uni-univalent salt not shifting the isoelectric point (9). Since the charge of proteins seems to depend mainly on the pH in the absence of salts, at any given pH a certain number of hydrogen ions over a time average are bound to the protein molecule. Assume then that v depends only on (κ) if the pH is fixed. ζ_E, and consequently v, which is proportional to ζ_E, will depend only upon κ if all other terms are considered constant, giving

$$v = v(\kappa)_{\sigma_{\mathrm{pH}} = \mathrm{const.}} \tag{7}$$

By assuming that σ remains constant we do not by any means imply that no change in σ occurs incidental to changes in κ. It is merely postulated that the change in v with σ, due to the variation of κ, is very small compared with the change in v due to explicit variation of κ. Addition of salt under these conditions, then, should cause only a diminution in v without a maximum in the curve. We have used our empirical form of equation 6

$$\zeta = \frac{Q}{Dr} \frac{1}{(2.4 + \kappa r)} \tag{8}$$

or

$$\zeta = \frac{Q}{Dr} \frac{1}{f(\kappa r)} \tag{8a}$$

to plot the theoretical form of the v–c curves in figure 9, by evaluating $f(\kappa r)$ for $r = 4 \times 10^{-7}$ cm. and various values of v for gelatin. Note the following points of interest in these curves.

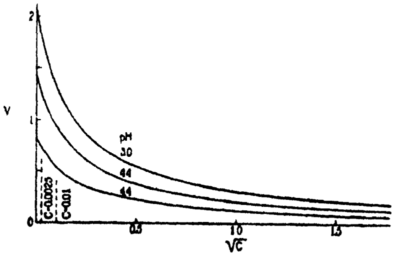

Fig. 9. Theoretical v–c Curves for Gelatin at Different Values of pH

The two short vertical dotted lines at the lower left corner show the limits of extrapolation when the pH is sufficiently low to have appreciable amounts of acid present.

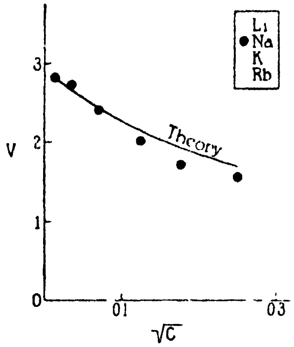

Fig. 10. Data of Loeb for Particles of Denatured Egg Albumin in 0.0002 M Sodium Hydroxide

The smooth curve is calculated by means of the theory here proposed

The curves should in reality not cut the ordinate at $c = 0$, for, in order to fix Q, a certain amount of acid must be present even though the concentration of protein and of salt is vanishingly small. In other words, v is always measured in the presence of a finite value of κ, which is given for strong acids by the concentration, and not by the mean activity, of the acid. The dotted lines indicate, for example, the limiting position of the ordinate for $c = 0.0025$ M and $c = 0.01$ M.

In more concentrated salt solutions the validity of equation 6 decreases; however, the curves indicate that v should be, as in the case of ions, still appreciable even in 4 M salt solutions. Technical difficulties at present prevent measurements of v in salts of this concentration, but values of the proper magnitude have been observed by Hitchcock in $M/25$ acetate buffers for gelatin and by the author for serum proteins in $M/7$ salt solutions. It would be most desirable to devise methods to discover if the available form of the theory is confirmed, in the prediction $v > 0$, by observations in concentrated salt solutions.

In figure 10 are values of v for denatured egg albumin particles in $M/5000$ sodium hydroxide. At this pH, in the absence of salt, v is rather high, 2.8μ per second. The smooth curve is the theoretical curve calculated by means of equation 8, taking $r = 2.2 \times 10^{-7}$ cm. and making the usual assumptions in regard to η and D.

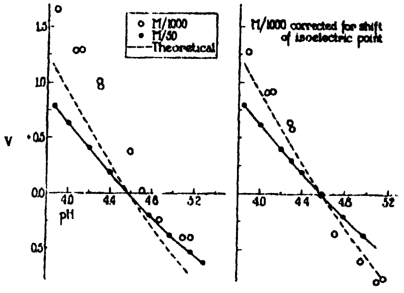

FIG. 11

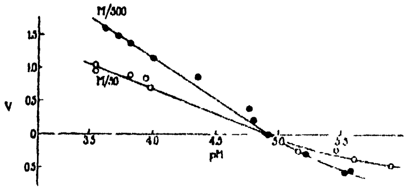

FIG. 12

FIG. 11. THE EFFECT OF THE CONCENTRATION OF ACETATE BUFFERS ON THE MAGNITUDE OF THE ELECTRIC MOBILITY

By correcting for the shift in the isoelectric point the effect of diluting the buffer is predicted.

FIG. 12. THE ELECTROPHORESIS OF GELATIN-COATED QUARTZ PARTICLES

The decrease in electrophoretic mobility is approximately predicted by the theory here proposed.

It is noteworthy that the courses of the theoretical and experimental curves are almost identical. Figure 11 gives the results of similar experiments and calculations for egg albumin in acetate buffers, a correction having been made for the shift in the isoelectric point with variation in c. Comparable results were obtained for egg albumin in hydrochloric acid and for gelatin in acetate buffers (figure 12). To summarize: by assuming that the electric charge of proteins is primarily determined by the hydrogen-ion activity of the medium and by making corrections when necessary for shift of the isoelectric point, it is possible to derive a simple relationship between v and the concentration of uni-univalent electrolytes. This relationship, namely, that v depends upon κ in a way which indicates that the decrease in the electric mobility of a protein ion with increasing concentration of a simple salt can well be understood by a diminution in the potential rather than in the charge, permits treatment of an electric mobility of an ion whose charge is given by a time average similar to an ion the charge of which is fixed.

Mueller (15) has treated the data of Freundlich and Zeh in a somewhat similar fashion. He showed that with the assumption of constant charge and constant average particle radius, the decrease in v found for an arsenic trisulfide sol could be accounted for simply by a decrease in the thickness of the double layer.

SUMMARY

During the course of an investigation of the chemical constitution of the surfaces of living cells, the ζ-potential and net charge density of surfaces in non-living models have been investigated. Two types of surfaces have been selected to carry out this analysis: (1) "inert" surfaces, the charge of which seems to be primarily dependent on forces of adsorption; (2) protein surfaces (amorphous), the charge of which is more intimately connected with ionization in a fashion similar to that observed for dissolved proteins.

(1) Calculations of the density of surface charge of graphite, quartz, collodion, cellulose, and paraffin oil in solutions of ions not reversing the sign of surface charge reveal a remarkable uniformity of behavior. In all cases, the complex form of the ζ–c curve is replaced by a simple type of curve resembling typical adsorption, with an initial steep slope and saturation at about 0.01 M[4].

(2) Assuming that the net charge of the protein surface primarily depends upon the pH, it is found that the course of the ζ–c curve is predicted by the simple theory that in dilute solutions the ζ-potential and consequently the electric mobility depends upon the thickness of the electric double layer under ideal conditions.

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[4] The writer wishes to point out that the relationship between the net charge density and the salt was apparently first pointed out by Abramson and Mueller at a meeting of the American Physical Society in 1932.

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PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. IX

SOME BINARY FREEZING POINT DIAGRAMS AND A STUDY OF THEIR IDEALITY

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Received October 8, 1934

It was recently pointed out (16) that the errors inherent in the usual Beckmann method of determining binary freezing point diagrams may be very considerable, causing a shift in the eutectic temperature and composition and in some cases causing false indications of compound formation. For the present investigation a number of systems which are reported in the literature as showing compound formation were reconstructed, using more recent and more reliable freezing point methods, with the added purpose of making a study of the degree of deviation from the ideal freezing point laws. The heats of fusion of four of the compounds involved were also experimentally determined.

PURIFICATION OF MATERIALS

In each case the compound was finally recrystallized, using a centrifugal filtration tube (13), until the sample gave cooling curves indicating suitable purity (1).

Eastman Kodak Co. benzamide was recrystallized from water four times and dried at 110°C. for two and one-half hours. *m*-Nitrophenol, made from *m*-nitroaniline, was supplied to us by Professor John Donleavy; it was fractionally distilled at 4 mm. pressure and then recrystallized from benzene. Acenaphthene, supplied to us by Dr. Lorenz P. Hansen, was vacuum sublimed, using a plug of glass wool to prevent particles from being carried into the sublimate mechanically; it was then recrystallized from alcohol. Kahlbaum's β-naphthylamine after fractional distillation at 12 mm. pressure proved to be suitably pure.[2] The *m*-dinitrobenzene used was purified as described previously (14).

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[1] Present address: Trinity College, Hartford, Connecticut.

[2] The final sample melted to a water-white liquid which gradually developed a pink coloration, probably due to a slight oxidation. A small sample was heated in an open tube in a Thelco oven at 120°C. for twenty hours. Although the liquid now had such a deep red color that it was practically opaque, its freezing point was only 0.14°C. lower than that of the pure product. Since this treatment was much more drastic than would be undergone by any freezing point sample, it was obvious that exclusion of air was unnecessary.

FREEZING POINT METHODS AND RESULTS

The freezing point measurements were made in part by the method and apparatus already described (15) and in part by the visual method of Johnston and Jones (5). The data obtained for three binary systems are given in table 1.

DISCUSSION OF FREEZING POINT DATA

A comparison of these results with those in the literature brings out the fact that binary freezing point data obtained by means of the Beckmann method are likely to be very much in error. The values here reported are in some cases as much as 10°C. above those reported by the previous authors. That the error is also partly due to the presence of impurities in the original samples is shown by the fact that the freezing points reported for the supposedly pure substances are often too low.

The system benzamide–*m*-nitrophenol affords a good example of a system in which the errors in the freezing point data caused a simple eutectic system to be mistaken for a case showing compound formation (8). There is actually only a single eutectic point, having the composition 56.5 mole per cent of *m*-nitrophenol and the freezing point 42.1°C. The results of Puschin and Rikovski (12)[3] for this system show fair agreement with ours, but they report their freezing points only to the nearest 0.5°C. and their eutectic halts to the nearest 1.0°C. Their diagram, which is based on melting point as well as freezing point measurements, falls above ours on the benzamide side, 0.8°C. higher for the pure substance and about 1.5°C. higher for the 70 mole per cent mixture. On the other hand, their eutectic temperature lies about 1°C. below ours. In order to verify our curve a sample containing 70.0 mole per cent of benzamide was agitated in a thermostat at 100.5°C., at which temperature it melted completely. Another sample containing 48.51 mole per cent of benzamide melted completely by the same method when the thermostat was at 57.2°C., but not when it was kept at 57.0°C. for fifteen minutes.

The diagram for the system acenaphthene–*m*-dinitrobenzene shows the formation of a stable 1:1 compound freezing at 71.9°C. with two eutectics, 68.7°C. and 66.5°C., at the compositions 36 and 68 mole per cent *m*-dinitrobenzene, respectively. The agreement of previous authors (3, 10) with our results is rather erratic. Most of their points fall below ours, but a few points on the acenaphthene branch and Giua's (3) values in the region of compound formation show good agreement. The freezing point reported by Giua for pure acenaphthene, 94.5°C., must certainly be in error, since our value, 93.3°C., was obtained from cooling curves which showed our sample to be amply pure.

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[3] In a previous paper (14) the binary freezing point data for the system naphthalene–*m*-dinitrobenzene were reported to show that Puschin's (11) supposed correction of the diagram of Kremann (6) was entirely incorrect. Although Puschin has evidently not seen our paper he has now (12) repeated the determinations on that part of the diagram which we called in question and he now agrees that a 1:1 compound does exist, but he gives 50.5°C. for the freezing point of the compound, which is 0.6°C. lower than our value. That there must still be a slight error in his results here is shown by the fact that the freezing point of his 1:1 compound is lowered by adding naphthalene but is not lowered by adding *m*-dinitrobenzene, so that there is no eutectic on that side of the 50:50 composition, but a "transition point." The questionability of such freezing point behavior has been pointed out by Kremann (7).

TABLE 1

Binary freezing point data

SYSTEM BENZAMIDE–*m*-NITROPHENOL		SYSTEM ACENAPHTHENE–*m*-DINITROBENZENE		SYSTEM β-NAPHTHYLAMINE–*m*-DINITROBENZENE	
Mole per cent of benzamide	Freezing point °C.	Mole per cent of acenaphthene	Freezing point °C	Mole per cent of β-naphthylamine	Freezing point °C.
100.0	127.2	100.0	93.3	100.0	109.5
90.6	120.5	94.5	90.5*	57.4	70.6 (55.0*c*)
70.7	101.1	89.2	87.5*	36.5	58.5 (53.5*c*)
58.1	80.1*	85.0	84.9*	29.7	66.4
56.3	74.5	83.8	84.3*	0.0	90.1
53.9	66.7	81.4	82.8*		
51.0	63.7*	73.4	78.0 (68.6*c*) (68.7*h*)		
46.7	51.7*	72.4	76.5*		
44.7	44.8*	67.3	72.6* (68.7*c*) (68.7*h*)		
		(64)	68.7		
44.2	—— (42.2*h*)†	61.6	69.9*		
43.7	42.3*	54.9	71.6*		
(43.5)	42.1				
43.3	—— (42.1*h*)	50.0	71.9		
40.6	48.9*	34.9	68.4*(66.7*h*)		
		(32)	66.5		
40.0	50.3*	28.0	70.2*(66.5*c*)		
35.5	58.4	26.3	71.8(66.4, 66.3*c*) 71.7*(66.5*h*)		
34.0	60.4*	17.5	78.4		
19.4	81.2	00.0	90.1		
00.0	96.8				

* By visual method.

† The temperatures in parenthesis are the temperatures of the eutectic halts. The letters *h* and *c* designate whether heating or cooling curves, respectively, were employed to determine the eutectic temperature. The percentages in parentheses are the estimated eutectic compositions.

Only three binary freezing points were determined for the system β-naphthylamine–*m*-dinitrobenzene. Our results show that the diagram reported by Kremann and Grasser (9) is essentially correct down to about 65°C., although their sample of β-naphthylamine had a freezing point 0.5°C. lower than ours. Our 58.5°C. point, however, is a little more than a degree higher than their values, and the eutectic halts which we obtained in the heating curves of the samples on the β-naphthylamine and the *m*-dinitrobenzene sides of the diagram were 55.0°C. and 53.5°C. as against their 53.3°C. and 51.8°C., respectively. The fact that there are two eutectics is additional proof that a compound forms, as Kremann and Grasser claim. There seems to be no basis for the statement (4) that the compound has an incongruent melting point.

TABLE 2

Heat content data for liquid and solid states

STATE	NO OF OBSERVATIONS	TEMPERATURE RANGE °C.	*a*	*b*	*c*	ΔH AT t_f CALORIES PER MOLE
			m-Nitrophenol			
Solid	5	74	−795	34.63	0.0680	5100
Liquid	5	45	2954	49.38	0.0581	
			Benzamide			
Solid	8	105	−652	27.17	0.1113	4900
Liquid	5	40	2323	46.83	0.0765	
			Acenaphthene			
Solid	7	71	−925	40.16	0.0852	4950
Liquid	6	50	2898	55.81	0.0447	
			β-Naphthylamine			
Solid	5	88	−880	37.71	0.1036	5250
Liquid	4	50	3616	41.67	0.1290	

THE HEATS OF FUSION

Direct calorimetric measurements of the differences between the heat contents of the liquid and solid forms of *m*-nitrophenol, benzamide, acenaphthene, and β-naphthylamine and the solid forms at 22°C. were made by the method described by Andrews, Lynn, and Johnston (2). Following their usage the heat content of the solid and of the liquid have been expressed by empirical equations, valid over a short temperature range in the neighborhood of the melting point, of the form $H = a + bt + ct^2$.

In this equation H is expressed in gram-calories per mole at $t°$, the heat content of the solid at 22°C. being taken as zero. The value of H for the liquid minus that for the solid is the heat of fusion, ΔH. For *m*-nitrophenol it is $\Delta H = 3748 + 14.76t - 0.0100t^2$; for acenaphthene it is $\Delta H = 3823 + 15.65t - 0.0404t^2$; for benzamide it is $\Delta H = 2975 + 19.66t - 0.0348t^2$;

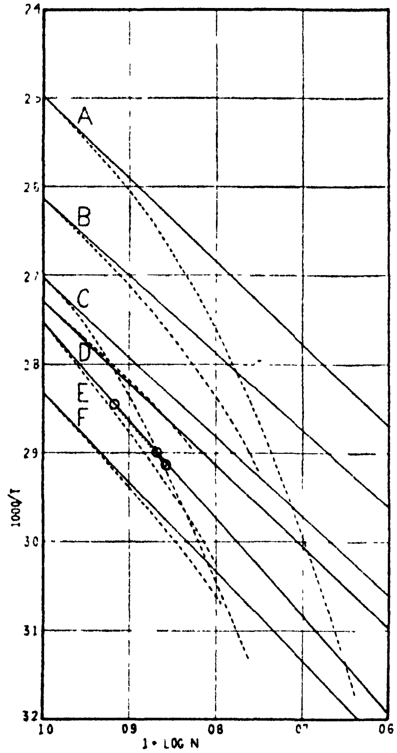

FIG. 1. PLOT OF 1000/T AGAINST 1 + LOG N FOR THE BINARY SYSTEMS AC, BE, DE, AND FE

A = benzamide; B = β-naphthylamine; C = *m*-nitrophenol; D = acenaphthene; E = *m*-dinitrobenzene; F = naphthalene. The full lines = ideal curves; the broken lines = experimental data. In curve A the second component was *m*-nitrophenol; in B, *m*-dinitrobenzene; in C, benzamide; in D, *m*-dinitrobenzene; in E ----, β-naphthylamine; in E ...., naphthalene; in E ⊙⊙⊙⊙, acenaphthene; in F, *m*-dinitrobenzene.

and for β-naphthylamine it is $\Delta H = 4496 + 3.96t + 0.0254t^2$. The values of ΔH calculated at the freezing point, t_f, are given in table 2.

DISCUSSION

The above data and those for the system naphthalene–*m*-dinitrobenzene (14) have been plotted in figure 1 to show how far the freezing point curves deviate from ideal behavior. The heavy straight lines represent the changes in $1000/T$ with $1 + \log N$ in case the ideal freezing point relationship

$$\frac{\mathrm{d} \ln N}{\mathrm{d}T} = \frac{\Delta H}{RT^2}$$

holds. In this equation, T is the freezing point in degrees Absolute of a sample of the composition N, expressed in terms of the mole fraction of the pure component crystallizing out at that temperature. ΔH, the heat of fusion of that component, is assumed to be constant[4] and equal to the calorimetrically determined values as given in table 2 and previously (2). The broken lines in figure 1 represent the experimental freezing point data for the systems in question. In all cases N was calculated without assuming any compound formation. The values for the compound region of the diagrams are of course not considered.

An examination of figure 1 reveals the very interesting but rather paradoxical fact that for the four binary systems under consideration the greatest deviation from ideality occurs in the case of that one for which the diagram shows no compound formation, viz., the system *m*-nitrophenol–benzamide. On the other hand, practical ideality is displayed by the system acenaphthene–*m*-dinitrobenzene, in which it is definitely known from the freezing point diagram that a stable 1:1 compound forms. The cause of these anomalies cannot be given definitely, but the *m*-nitrophenol–benzamide case could be explained by assuming that a compound does form but that solubility relations are such that it does not crystallize out.[5]

In both of the other systems the deviation is such as would be normally expected in the case of compound formation. In all four binary systems the extent of deviation can be seen to be roughly the same for the two branches of the diagram.

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[4] Since the expression for ΔH in terms of T is not applicable over the wide range in question.

[5] If we assume ideal freezing point lowering by the compound, the proportion present at the eutectic point can be calculated from the deviation on each side of the diagram. Thus a mixture made from 0.433 mole of benzamide and 0.567 mole of *m*-nitrophenol could be calculated from the ideal benzamide curve to have the actual composition 0.133 mole of benzamide, 0.267 mole of *m*-nitrophenol, and 0.300 mole of 1:1 compound. This shows very poor agreement, however, with the corresponding results for the same point calculated from the ideal *m*-nitrophenol curve, viz., 0.052, 0.186, and 0.381, respectively.

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FERRIC OXIDE AND AQUEOUS SULFURIC ACID AT 25°C.

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INTRODUCTION

In a series of papers by Recoura (7), another series by Scharizer (8), and in papers by Niggli and Faesy (5), Grimm and Ramdohr (3), Weinland and Ensgraber (10), and by others, there are described many compounds containing varying proportions of ferric oxide, sulfur trioxide, and water. That all are *stable* solids under the conditions described is more than doubtful, but any of them may have been actually realized. Metastable equilibria are common and persistent in the system, Fe_2O_3–SO_3–H_2O, where diffusion is slow, liquids viscous, crystallizing forces weak, supersaturations common, and colloidal dispersion frequent.

Cameron and Robinson (2), Wirth and Bakke (11), and Appleby and Wilkes (1) found that at 25°C. the solubility of ferric oxide in aqueous solutions increased steadily with increasing concentration of sulfuric acid to a well-defined maximum. As to the concentrations at this maximum, they disagree among themselves, with earlier determinations by Scharizer, and with those to be given presently. All observers found the solid phases in contact with the liquid solutions containing less than 26.4 per cent sulfur trioxide varied continuously in content of ferric oxide and sulfur trioxide. Cameron and Robinson and Appleby and Wilkes regarded the solids as members of a series of solid solutions, while Wirth and Bakke thought they formed two series with an ill-defined transition point. They avoided defining them as solid solutions. Similar results were obtained at 18°C. by Appleby and Wilkes. Posniak and Merwin (6), who worked on the system at higher temperatures but *not* at 25°C., objected to the conclusion that these solids form a series of solid solutions, and regarded them as adsorption complexes.

With increasing concentration of sulfuric acid beyond that at which the ferric oxide is most soluble, the solubility of the ferric oxide decreases, at first very rapidly, then more and more slowly. At very high concentrations of sulfuric acid, there is no detectable iron in the liquid phase and apparently no water in the solid. There are several transition points with change in the composition of the solid in contact with the liquid solutions. So much is agreed upon by all observers. There is, however, very wide divergence among these observers regarding position of the solubility curves and transition points and the composition of the corresponding solid phases.

EXPERIMENTAL WORK

Preparation of residues

It is quite impracticable to make complete separations of solids from their corresponding mother liquors in this system; hence the necessity of using indirect methods to determine the composition of the solids. The "telltale" method of van Bijlert (9) was discarded, since a suitable telltale was not found. The method of "residues" was employed by Wirth and Bakke, plotting their results on the right-angled isosceles triangle and by Appleby and Wilkes, plotting on the 60°-angled isosceles triangle (the conventional equilateral triangle). Owing to the character of the tie line fans or fasceaus in this system, the right-angled isosceles triangle is preferable in the interest of clarity; also, statement of the results in grams rather than in reacting weights. Undoubtedly, a principal factor making for confusion in the work of previous investigators was their inability to separate the mother liquors from the residues with any approach to completeness, with consequent uncertainties in the directions of the tie lines. In this investigation the solutions were filtered through multiple paper mats under several hundred pounds pressure. The residues thus obtained were dry to the touch and friable, though yet containing appreciable amounts of adhering mother liquor.

Results obtained in a study of six series of solutions

Series 0. Six series of solutions were studied (see data in table 1). In series 0, the bottles containing the suspensions were heated in a water bath until the contents were completely liquefied. On cooling, they were continuously agitated in a large constant temperature bath. From time to time during a period of about nine months, they were removed from the bath to transfer some of the solid from one bottle to another for a thorough re-seeding of each. Finally they remained in the bath four to five months before the contents were analyzed.

The plot shows the liquid solution data falling on or very close to a straight line, and the tie lines between these and the corresponding residue data form a spreading fan, indicating a series of solid solutions with ferric oxide (probably hydrated) as one limiting member, and, as the other limiting member, a compound approaching in composition the definite solid ($Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$) appearing at a concentration of sulfuric acid higher than that at which the ferric oxide is most soluble.

Series A. The solid employed in preparing series A was made by oxidizing with nitric acid a solution of ferrous sulfate and ferric chloride in equally

TABLE 1

Composition of solutions, corresponding residues, and solid phases in the system Fe_2O_3–SO_3–H_2O at 25°C.

SERIES	SOLUTIONS		RESIDUES		SOLID PHASES
	SO_3	Fe_2O_3	SO_3	Fe_2O_3	
	per cent	*per cent*	*per cent*	*per cent*	
0	9.59	7.64	16.70	47.20	Solid solution
	23.38	18.76	29.04	49.36	Solid solution
	25.45	20.04	31.56	43.27	Solid solution
	25.62	20.19	31.61	45.31	Solid solution
	26.37	20.45	35.53	30.37	Solid solution
	27.01	18.32	36.31	28.55	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
A	12.55	9.86	11.59	71.73	Solid solution
	18.51	13.87	10.46	82.54	Solid solution
	23.96	17.19	7.77	79.89	Solid solution
	28.95	17.95	4.54	83.80	Solid solution
B	12.98	10.19	15.55	51.94	Solid solution
	19.21	15.52	25.82	40.98	Solid solution
	25.22	19.08	26.15	41.27	Solid solution
C	3.55	2.45	7.23	65.25	Solid solution
	6.83	4.86	7.81	63.37	Solid solution
	13.79	9.91	29.85	55.56	Solid solution
D	8.02	4.76	2.67	81.60	
	18.17	12.33	5.66	77.57	
	24.67	16.67	5.02	67.59	
	30.07	18.98	12.49	77.88	
	26.4	*20.5*			Solid solution and $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
E	26.71	19.06			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	26.60	18.76	36.35	27.95	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	26.85	18.21			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.11	17.70	36.92	27.61	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.45	17.31			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.45	17.16			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.00	16.70	36.93	28.01	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.20	*16.4*			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$ and $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.88	15.94	37.74	28.67	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.95	15.40	37.01	27.52	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	29.15	15.10	38.15	27.55	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.28	14.49	39.26	25.06	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.30	13.92	38.39	23.90	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.88	12.18	38.84	23.85	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.80	11.90	38.56	23.88	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$

TABLE 1—*Concluded*

SERIES	SOLUTIONS		RESIDUES		SOLID PHASES
	SO_3	Fe_2O_3	SO_3	Fe_2O_3	
	per cent	*per cent*	*per cent*	*per cent*	
E	28.92	11.06	38.78	23.53	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	29.00	10.87	39.66	24.63	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	29.64	9.31	39.64	24.31	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	32.1	*7.2*			$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.06	6.96	47.03	22.40	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.10	6.82	48.38	23.39	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.68	4.70	44.09	23.26	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
			44.25	23.58	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	34.34	2.03	46.76	20.35	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	38.72	0.26	47.35	19.13	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	45.28	0.06	48.14	14.40	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	51.40	0.03			$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	56.79	0.03			$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	30.3	*14.7* (Metastable)			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$ and $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	30.96	10.34	41.50	25.62	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.20	9.55	41.75	25.78	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.47	8.95	42.62	26.43	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.54	8.94	42.26	26.32	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.8	*8.4* (Metastable)			$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.88	8.11	47.79	23.99	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.83	7.97	45.76	24.22	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.86	7.76	46.46	22.33	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$

molar quantities, drying, and washing the residue to remove chlorine and nitric acid. It was a grayish tan colored product, containing 30.60 per cent sulfur trioxide and 58.45 per cent ferric oxide. The suspensions were agitated at constant temperature for four months, the liquids analyzed, and agitation resumed for three months, and the liquids again analyzed. No significant change in the composition of the liquid phases having taken place, the corresponding residues were prepared and analyzed. The data for the two liquid solutions of lowest concentration fall on the right line plotted from series 0. The data for the solution of next higher concentration fall somewhat below the line, and the data for the solution of highest concentration fall in another field. The tie lines all slant towards the axis of ferric oxide composition. It appears that this series had not come to final equilibrium. For the sake of clarity the data are not shown in the accompanying chart.

Series B. The solid used in preparing series B was made by bringing into solution with hydrochloric acid a mixture of ferric oxide and ferric sulfate in the proportion of 2 moles to 1, slowly evaporating to dryness, and washing the residue until free from chlorides. It was light yellowish tan in color and contained 26.89 per cent sulfur trioxide and 54.95 per cent ferric oxide. The solutions were analyzed after four months and again after seven months agitation at constant temperature. No significant changes having taken place, the residues were prepared and analyzed. The data for the liquids fall on the right line found from series 0 and the corresponding tie lines form a spreading fan.

Series C. The solid used in preparing this series was obtained by extracting some of the solid prepared for series B with dilute ammonia water and washing the residue free of ammonia. It was dark red in color and contained about 1 per cent sulfur trioxide and 94.2 per cent ferric oxide. The series was agitated for seven months at constant temperature, and the liquids analyzed at the end of four months and seven months. No significant changes having taken place meanwhile, the residues were prepared and analyzed. The results harmonized with those obtained from series 0 and B.

Series D. In preparing this series, a standard brand of analyzed ferric oxide was employed. It was blood-red in color. The series was agitated for seven months. The data for the liquids give points somewhat below the right line plotted from the results obtained from series 0, B, and C, the discrepancy being the greater the greater the concentration. The tie lines for solution and residues are important. They all slope towards the axis of ferric oxide, and show the solid phase was essentially ferric oxide in each case, slowly absorbing sulfur trioxide and water. They do not converge to a point nor give any evidence of the formation of a definite compound.

Series E.[1] For this series several solids were prepared, hydrated ferric oxides and basic ferric sulfates. They were prepared from aqueous solutions, and great care taken to remove contaminations and to avoid overheating. The suspensions were agitated continuously at 25°C. for seventeen months, then allowed to settle for two months, analyses of liquids and residues being made during the latter period. A plot of the data for liquids and corresponding residues shows four solubility curves were realized: one, corresponding to stable conditions only; one, to metastable conditions only; and the other two partly to stable and partly to metastable conditions. Transition points were found with approximate accuracy by interpolation. Attempts to realize them experimentally are impracticable.

The fasceau or bundle of tie lines in three cases is too narrow to permit a definite convergence, so the composition of the solid phase in equilibrium with the several solubility curves was determined in another way. Since, in any group of points representing residues, the individual points lie close together, it may be assumed that the ratio of ferric oxide to sulfur trioxide in them approximates that in the corresponding solid. Actually, the residues all contained a slight excess of acid, due to adhering mother liquor. A straight line through the origin and at the angle whose tangent corresponds to this ratio, must pass through the point corresponding to the composition of the solid phase. This point must lie within the limits of the fasceau and must also correspond to a rational formula. The procedure proved to be easy and satisfactory in application.

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[1] The analytical data for series E are taken from a dissertation submitted by E. W. Constable in May, 1934, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The authors of this paper are responsible for the interpretation of the data.

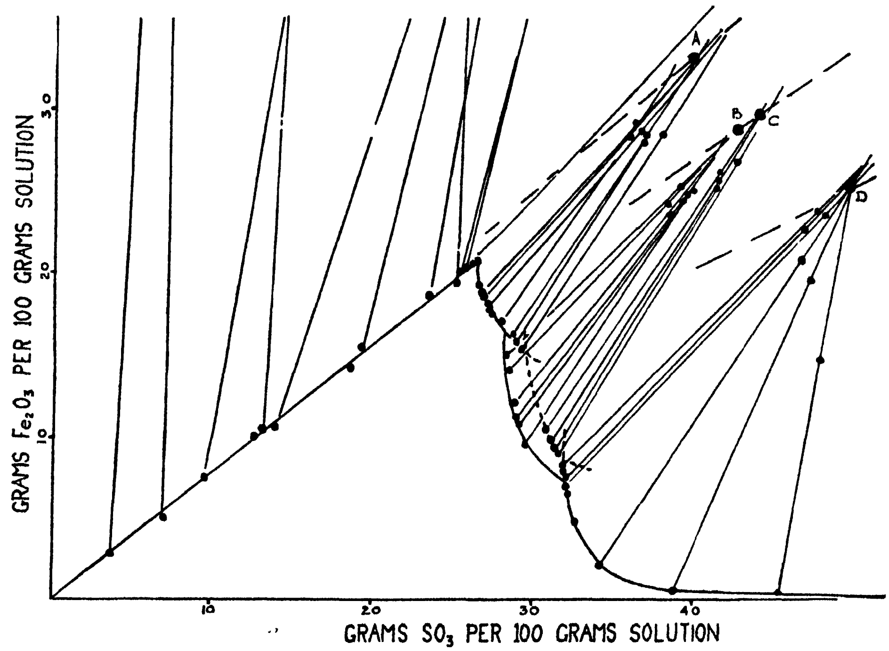

FIG. 1. SOLUBILITY CURVES, RESIDUES, TIE LINES, AND SOLID PHASES IN THE SYSTEM FERRIC OXIDE–AQUEOUS SULFURIC ACID AT 25°C.

A, $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$. B, $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$. C, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$. D, $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$.

Specific gravity and viscosity of solutions

To investigate further the possible existence of a transition point in the solubility curve corresponding to the series of solid solutions, specific gravity determinations of the liquid phases were made with a Westphal balance. The results are assembled in table 2. When plotted against content of sulfur trioxide or ferric oxide, the points corresponding to the solutions presumed to have reached equilibrium fall on a smooth curve passing through the origin. A curve passing through the most possible of all points does not indicate any intermediate transition point.

For the same purpose viscosities were estimated by timing the rate of flow of the solutions through a capillary and comparing with the rate of flow of water through the same capillary. These results are also assembled in table 2. When plotted they fall on a smooth curve, nor is there any indication of an intermediate transition point. There is some uncertainty attaching to the higher viscosities, a solution from which the dispersed solid has long settled showing a slightly higher viscosity than one which has recently been vigorously agitated with the suspension.

Colloidal dispersions

Abnormally high viscosities, with other observations, suggested that ferric oxide, or substances corresponding to basic sulfate formulas, might be dispersed as sols. Therefore solutions in contact with their respective solid phases were set aside in a quiet place in the laboratory for a year. Probably the temperature variation was within the limits 25° to 30°C.

TABLE 2

Comparison of specific gravity and coefficient of viscosity with sulfur trioxide and ferric oxide content of aqueous solutions of ferric hydrates at 25°C.

PER CENT OF		SPECIFIC GRAVITY	VISCOSITY COEFFICIENT	PER CENT OF		SPECIFIC GRAVITY	VISCOSITY COEFFICIENT
SO_3	Fe_2O_3			SO_3	Fe_2O_3		
3.55	2.45	1.052	0.0095	18.51	13.87	1.364	0.0206
6.83	4.86	1.104	0.0101	19.21	15.52	1.397	0.0241
8.02	4.76	1.118	0.0101	23.96	17.19	1.500	0.0501
12.55	9.86	1.229	0.0127	24.67	16.67	1.471	0.0406
12.98	10.19	1.242	0.0129	25.22	19.08	1.550	0.0756
13.79	9.91	1.243	0.0136	28.95	17.95	1.590	0.0930
18.17	12.33	1.328	0.0187				

In no case was the solution completely empty, optically, although the transmitted light beam showed but little solid to be present. Microscopic examination of these solutions with a dark field illumination showed, in each case, particles exhibiting Brownian movements. In some cases these particles appeared to have definite forms, but were too small to admit of precise description, and their total mass in any case must have been negligible in comparison with the dissolved constituents. No doubt the presence of colloidal dispersions may account, in part at least, for the difficulties and discrepancies noted by investigators of this system, but its importance has been exaggerated.

X-ray spectrographs of the solids

Diffraction x-ray spectrograms were made of the residues corresponding to the series of solid solutions; also, for comparison, of ferric oxide and of the normal sulfate, $Fe_2O_3 \cdot 3SO_3$, made by the directions of Recoura. Recording the many readings of the lattice spaces would require a table beyond reasonable dimensions. The photographs seem to fall, more or less clearly, under one or the other of two types, which may be designated as alpha and beta. The alpha type approaches the spectrogram for ferric oxide, while the beta type approaches that for the normal sulfate. The distinction is none too sharp, for certain lines appear in both the ferric oxide and the normal sulfate spectrograms, and some lines from both are to be found in the individual spectrograms of most of the residues. Two of these, because of the small number of lines which can be definitely measured, are in doubt. Practically every line they show which can be definitely measured is found in the spectrogram of ferric oxide, also in that of the normal sulfate. In table 3, the first column records the series to which the residue belongs; the second the mole ratio of sulfur trioxide to ferric oxide in the residue as shown by analysis; the third column the type of spectrogram given by the residue; and the fourth column the slant of the tie line, whether to the left towards the ferric oxide axis, or contrariwise. Clearly, the two sets of observations are in reasonable agreement. Further study of the observations may reveal more definite results, but for the present it may be said that the x-ray spectrograms support the view that the residues are mixtures. Since we may have but one solid phase in the residue, under equilibrium conditions, each of these mixtures would seem to be a member of a series of solid solutions. It is reasonable to think one limiting member of the series is ferric oxide or a hydrate of it. The composition of the other limiting member of the series lies between $Fe_2O_3 \cdot 1.25SO_3 \cdot nH_2O$ and $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$; and probably near the latter.

DISCUSSION

The solubility of ferric oxide at 25°C. was found to be directly proportional to the concentration with respect to sulfuric acid, in solutions containing less than 26.4 per cent sulfur trioxide. The results of previous investigators are in fair agreement. The rate at which equilibrium was reached between the solutions and the corresponding solids was slow, the more so in the more viscous and highly concentrated solutions. The rate of solution was found to be dependent on the composition, the physical character, and previous treatment of the solid brought into contact with the liquid.

The conclusion of Wirth and Bakke that there is a transition point corresponding to the liquid containing 22.1 per cent sulfur trioxide and 19.7 per cent ferric oxide was disproved. The stable solids in equilibrium with the liquids were found to form one single series of solid solutions, one limiting member being ferric oxide probably somewhat hydrated and the other probably approaching in composition the basic salt $Fe_2O_3 \cdot 2.5SO_3 \cdot$

$7H_2O$, which is the stable solid when the liquid reaches a concentration beyond 26.4 per cent sulfur trioxide. The residues in contact with two of the liquids in series B approximated the composition of a basic salt $Fe_2O_3 \cdot 1.25 SO_3 \cdot nH_2O$, and the chart shows the limiting solid is yet more acid in composition. Posniak and Merwin argue these solids to be adsorption complexes because they follow Freundlich's law. They do, and should if they be solid solutions. They do not appear to be crystalline, but all solid solutions are not mixed crystals. It would be necessary to assume unbelievably thick films if they be adsorption complexes. The character of the tie lines would seem to prove that the solids are solutions, a view supported by consideration of the x-ray spectra.

Increasing the concentration of sulfur trioxide beyond 26.4 per cent, the new solid phase appearing was found to be the basic salt, $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$. Wirth and Bakke reported it as α-copiapite, $Fe_4S_5O_{21} \cdot 18H_2O$, the laboratory-made product having been studied by Scharizer and the naturally occurring product by Linck, Geroth, and McCaughey (4). They also reported a β-copiapite $Fe_3(OH)(SO_3)_4 \cdot 13H_2O$ as stable solid for a part of the solubility curve, although there is no inflection in the curve when the beta variety replaces the alpha salt. They were probably misled by analyses of their very wet residues. Appleby and Wilkes reported the stable solid over this range of concentration to be a basic salt $5(FeO_3 \cdot 3SO_3) \cdot 2Fe_2O_3$. Very wet residues and misplaced confidence in the use of the equilateral triangle misled them.

TABLE 3

Comparison of data from tie lines and spectrograms of residues for the system Fe_2O_3–SO_3–H_2O *at 25°C.*

SERIES	COMPOSITION	TYPE	SLANT	SERIES	COMPOSITION	TYPE	SLANT
A	0.108	Alpha	Left	D	0.320	Alpha	Left
D	0.146	Alpha	Left	A	0.330	Alpha	Left
D	0.149	Alpha	Left	B	0.580	Beta	Right
A	0.194	Alpha	Left	C	1.08	Beta	Right
C	0.227	?	Right	B	1.26	Beta	Right
C	0.247	?	Right	B	1.27	Beta	Right
A	0.250	Alpha	Left				

Over the next range of concentration of sulfuric acid the solid phase in contact with stable liquids was found to be the normal salt $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$. This salt, known as coquimbite in natural occurrences, was reported by Wirth and Bakke, but Appleby and Wilkes reported the stable solid over this range of liquid concentrations to be the heptahydrate, $Fe_2O_3 \cdot 3SO_3 \cdot 7H_2O$.

Over a yet higher range of concentration of sulfuric acid, the stable solid was found to be the acid salt $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, which was reported by Wirth and Bakke and by Appleby and Wilkes. The former reported it to be replaced by the trihydrate in contact with solutions containing upwards of 34 per cent sulfur trioxide, which the present investigation contradicts.

Wirth and Bakke found the solubility curves corresponding to the basic salt and the acid salt to extend into metastable regions. The present investigation goes further. A complete metastable solubility curve was found, one transition point quite definitely, the other with fair precision, and the solid phase in equilibrium with the solution represented by the curve was shown to be the normal salt, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$.

It is futile to compare the data reported by previous investigators for the solutions in contact with the above cited solids, the several sets of observations disagreeing widely.

Finally, attention is directed to the fact that in no case does the right line connecting the origin with a point representing a definite salt intersect the solubility curve corresponding to that salt. There are no congruent points in the system. This fact explains many of the difficulties reported in earlier investigations.

SUMMARY

In regard to the system Fe_2O_3–SO_3–H_2O at 25°C. the following observations have been made:

1. Ferric oxide, Fe_2O_3, has a maximum solubility of 20.5 g. in a solution containing 26.4 g. of sulfur trioxide.
2. Solution is slow, depending much upon the composition, physical characteristics, and previous history of the solid brought into contact with the solution.
3. Approach to equilibrium is slower the more concentrated, therefore the more viscous, the liquid phase.
4. From zero concentration to 26.4 per cent sulfur trioxide the solubility of ferric oxide is directly proportional to the concentration in sulfur trioxide. The solids in contact with these solutions form one continuous series of solid solutions.
5. Solubility curves were found in equilibrium with the solids: $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$, $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$, and $F_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The system of solutions in equilibrium with solid $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$ was found to be metastable. Transition points were determined by interpolation.
6. There are no congruent points in the system.

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THE ATOMIC MASS OF POTASSIUM. II

THE POTASSIUM CHLORIDE–SILVER RATIO

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The following report summarizes a determination of the potassium chloride–silver ratio by the new and now fully developed standard solution method (2).

PURIFICATION OF REAGENTS

The general criterion of acceptable purity for any reagent used in this work was that it should introduce no impurities equivalent to more than 0.005 mg. of silver into any single analytical system or 1500 g. of standard solution.

Potassium chloride. The potassium materials were obtained from five different manufacturers. The salts were purified by rapid crystallization from hot or cooling solutions in 500-cc. platinum dishes. In a few of the early crystallizations, and whenever free chlorine was present in the solutions, quartz vessels were used. As a general rule (applying also in the purifications of silver, lime, sugar, potassium nitrate, sodium nitrite, and ammonium chloride) small head and tail fractions were rejected in each crystallization or precipitation. The central fraction was always drained for about fifteen minutes at 1500 R. P. M. in a centrifuge attachment in which the salt was inclosed entirely in platinum. Fusions which were part of the potassium chloride purification were made in a 180-cc. platinum cup in an electrically heated 200-cc. porcelain beaker. After these fusions the salt was dissolved in water and filtered through a platinum Munroe crucible.

Sample 1 (40 g.) was separated from a 500-g. quantity of potassium oxalate from a Norwegian source. This material was crystallized six times, changed to the chloride by one treatment of the solution with chlorine gas, crystallized once, and fused. Sample 2 (42 g.) was obtained from a kilogram of potassium nitrate from a German source. This material was recrystallized ten times, then precipitated three times from solution with hydrogen chloride gas. After each of the three precipitations the potassium chloride was fused and crystallized once from water. Sample 3 (43 g.)

was taken from 500 g. of potassium chlorate from a German source. The chlorate was recrystallized ten times and carried cautiously through the two stages of decomposition to a state of clear fusion. Rejected liquors from subsequent crystallizations (*vide infra*) contained less than 0.01 mg. of chlorate and perchlorate. Sample 4 (67 g.) was separated from 500 g. of potassium chloride from a German source. After one crystallization from water the material was precipitated twice from solution with hydrogen chloride gas. After each precipitation the salt was crystallized once from water, fused, and again crystallized from water. It was next crystallized from constant-boiling hydrochloric acid, then from water, and fused. Sample 5 (78 g.) was taken from an 1100-g. quantity of 98 per cent muriate of potash from Searles Lake, California. This salt was crystallized once from dilute aqua ammonia, twice from water, and once from 1 *M* hydrochloric acid made from recrystallized Searles Lake potassium chloride. It was then crystallized eight times from water and fused.

To complete the above purifications, each of the five potassium chloride samples was crystallized three times from water, filtered through a Munroe crucible, and then crystallized, centrifuged, and dried with especial care to avoid the introduction of platinum scrapings. The centrifuged crystals were dried in a platinum dish for three hours at 180°C., and then desiccated over broken pieces of fused potassium hydroxide at pressures less than 0.002 atmosphere for at least three days.

By weighing all of the platinum before and after use in these final procedures it was found that a maximum of 0.14 mg. of platinum could have been present in the five samples (270 g.).

Silver. Three silver samples were purified independently at different times. Sample 1 (526 g.) was prepared from 1500 g. of C. P. silver nitrate. After one crystallization from water this material was precipitated from saturated solution by slow addition of 15 *M* nitric acid, using 0.38 cc. of acid per gram of silver nitrate. The crystallization and precipitation with acid were repeated, and the 925 g. of material remaining was made up to a liter with water and neutralized with ammonia. The dissolved salt was then reduced to silver by addition of 1.5 liters of solution made by neutralizing formic acid with ammonia, using 0.50 cc. of 78 per cent acid per gram of silver. The mixture was kept slightly alkaline with ammonia and warmed toward the end of the reduction. Sample 2 (465 g.) was prepared from 750 g. of heterogeneous silver residues, which were reduced to silver with zinc and sulfuric acid. The silver was thoroughly washed and dissolved in 7.5 *M* nitric acid, using 1.85 cc. of acid per gram of silver. It was next precipitated as silver chloride. This compound was reduced to silver with a warm concentrated solution containing 1.80 g. of sucrose and 0.50 g. of sodium hydroxide per gram of silver. The silver was thoroughly washed, dried, and fused on lime in a current of methane. The solution in nitric acid, precipitation as chloride, reduction to silver, and fusion were then repeated. The etched silver bars were dissolved in nitric acid and reduced to silver with ammonium formate solution containing an excess of 0.5 cc. of 5 *M* aqua ammonia per gram of silver. Sample 3 (528 g.) was prepared from a kilogram of C. P. silver nitrate. The material was precipitated as silver chloride and recrystallized once from freshly prepared 5 *M* aqua ammonia. The crystals were digested in 6 *N* hydrochloric acid and aqua regia, washed, and reduced to silver with sucrose and sodium hydroxide. The 565 g. of silver remaining was washed, fused, etched, dissolved in nitric acid, and made up to 8 liters in a solution containing 100 g. of excess ammonia. The compound was reduced to silver by addition of a solution made by collecting 300 g. of sulfur dioxide in 1.5 liters of solution containing 160 g. of ammonia. The mixture was warmed to complete the reduction.

Occasional filtrations were an essential part of the above purification schemes. All precipitations were made from dilute solutions. Precipitated silver and silver chloride were washed twenty to thirty times with 1-liter portions of water.

To complete the above purifications each of the three silver samples, supported on lime in a current of hydrogen, was fused in a quartz muffle into 50-g. to 100-g. bars. The bars were deeply etched, then transported at 0.02 to 1.0 amperes across a cell made entirely of quartz. The electrolytic crystals were thoroughly washed, dried in quartz, and fused into 0.1-g. to 10-g. buttons, supported on lime in a 5-ampere current of electrolytic hydrogen, in a clean quartz muffle (3).

The formation of silver with the necessary smooth unbroken surface was favored by the following conditions. The current was first passed at 8.5 amperes, then held at 9.2 amperes until the silver had melted. After five to fifteen minutes, during which the furnace was rocked occasionally, the current was lowered to 7.0 amperes until the silver had solidified. The silver was cooled completely before removing it from the hydrogen atmosphere. The buttons were deeply etched, washed, dried in quartz, and finally heated for two hours in a quartz tube at 400° to 500°C. in a 2×10^{-8} atmosphere vacuum. They were kept in desiccators over fused potassium hydroxide until ready for use.

Potassium nitrate. Two samples of potassium nitrate were each crystallized ten times from water. When portions of these samples were subjected to nephelometric tests capable of revealing unmistakably one part in a million of silver or its chloride equivalent, they showed no trace of these impurities. Approximately 9.4-g. portions of the material, fused in platinum and weighed to the nearest 0.1 mg., served as the starting point in the synthesis of the standard solutions.

Lime. Three samples of lime were prepared from C. P. calcium nitrate by variations of a procedure including several crystallizations of the nitrate, electrolysis to remove traces of iron or heavy metals, and two precipitations from solution with freshly prepared ammonium carbonate solution, followed by ignition in a quartz muffle.

Water. The water used in the purification and analysis of samples 2 and 4 of the potassium chloride was obtained by distilling the ordinary distilled water of the laboratory without addition of reagents until the main fraction had a specific conductance of about 0.20×10^{-6} ohm^{-1} cm.$^{-1}$ when treated with pure nitrogen at 25°C. For all other work water from the same source was redistilled in succession from dilute alkaline permanganate solution and very dilute sulfuric acid.

Other reagents. Phosphorus pentoxide was resublimed in a current of purified oxygen in an all-glass apparatus. Aqua ammonia, formic acid, nitric acid, and hydrochloric acid were purified by one to three distillations of the C. P. concentrated or suitably diluted reagents in quartz apparatus. Sugar, sodium nitrite, and ammonium chloride were crystallized once from water. Solutions of sodium hydroxide were filtered through a Munroe crucible and electrolyzed in a platinum dish until free from iron and heavy metals. Commercial methane, carbon dioxide, chlorine, sulfur dioxide, oxygen, nitrogen, and hydrogen were washed in trains of towers containing glass pearls covered with suitable reagents. The hydrogen used in the final silver fusions was prepared by electrolysis of 20 per cent sodium hydroxide solution and purified by passage in succession through six 30 cm. × 2.5 cm. towers of 3-mm. pearls covered with concentrated sulfuric acid, a tube containing 50 cm. of No. 27 platinum wire carrying a current of 5.2 amperes, an 80 cm. × 2.5 cm. tube containing pieces of fused potassium hydroxide, and a 40 cm. × 2.5 cm. tube of glass pearls mixed with phosphorus pentoxide. The same train was later used in drying the purified nitrogen employed in the fusion of the potassium chloride. In analyses 3 to 7 inclusive, nitrogen was prepared by dropping a solution of sodium nitrite into a hot solution of ammonium chloride; in the other analyses the gas from a commercial tank was used. Both gases met the necessary requirements for purity and dryness when treated in succession with acid permanganate solution, hot copper gauze, potassium hydroxide solution, concentrated sulfuric acid, fused potassium hydroxide, and resublimed phosphorus pentoxide.

THE ANALYSES

Weighings were made at temperatures from 22°C. to 26°C. with relative humidities between 8 and 54. To eliminate a certain group of potential weighing errors the substitution method was extended to include a recheck of the first rest-point. The (true) mass values for the entire set of Class M weights were determined three times during the work, once at the U. S. Bureau of Standards. The greatest discrepancy in the three calibrations was one of 0.006 mg. in one of the platinum fractionals. For each weighing the air density was calculated from temperature, pressure, and psychrometric observations. Vacuum corrections were applied through the expression: $m = s + d(V_m - V_s)$, in which m is the mass of the object weighed, s the mass of the corresponding weights, with rider and rest-point corrections applied, d the air density, V_m the volume of the object, and V_s the sum of the volumes of the weights. The volumes of the gold-plated brass weights were determined by hydrostatic weighings; the other volumes were calculated with the aid of the densities: Pt, 21.45; Al, 2.70; KCl, 1.989; Ag, 10.49; KNO_3, 2.11. Counterpoises were used in weighing the fused salts in their platinum containers. A statistical examination of the rest-point data in relation to the sensitivity of the balance showed that the recorded weights are significant on the average to about 0.005 mg.

For each analysis a 7.1-g. sample of potassium chloride was fused in a 15-cc. platinum-rhodium boat in another quartz muffle of the same type used in the silver fusions, in a current of dry nitrogen. The muffle was lined with 0.001 in. sheet platinum.

The weighed salt was dissolved out of the boat and made to a volume of 500 cc. In analyses 7 to 15 the salt samples were first tested for alkali in a volume of 50 cc., by a modification of the method of Hönigschmid (1); the 0.05 cc. of 0.004 M chloride-free methyl red solution introduced in this procedure apparently had no effect in subsequent operations.

A weighed quantity of silver was next dissolved in a calculated excess of 7.68 M nitric acid in the 3-liter Pyrex analysis flask and the solution was warmed to remove nitrous fumes, except in analysis No. 15.[1] The solution was made up to 500 cc. and the salt solution was added drop by drop with constant rotation of the analysis flask, in the light of a Series OA Wratten Safelight. In analyses 3, 12, 13, 14, and 15, however, the silver chloride was precipitated by simultaneous drop by drop addition of the two 500-cc. solutions to 200 cc. of water, with constant rotation. In these five experiments the precipitation thus took place at concentrations which could scarcely have exceeded 0.0005 M, on the average.

In each case the analytical system was made up with water to contain 1520.7 g. of solution per 10.0000 g. of silver (9.3718 g. of potassium nitrate) and allowed to stand at room temperature for fifteen to fifty days, with occasional vigorous shaking. The acid concentration of the analytical solution was adjusted to 0.3025 molar after titration of a portion with standard alkali, and the system was brought to equilibrium by at least three days cooling at 0°C., with gradual reduction of the shaking to a minimum.

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[1] Nitrite, which would seriously affect the potentiometric analyses, is best removed at this stage. In analysis No. 15 it was found that nitrite is removed only very slowly by bubbling nitrogen or oxygen through the analytical solution.

The supernatant analytical liquid was analyzed both nephelometrically and potentiometrically for silver and chloride by comparison of filtered samples withdrawn at 0°C. with standard solutions having very nearly the same composition (2, 4). In the nephelometric analyses the standard and test solutions were at exactly the same temperature, i.e., room temperature; in the potentiometric analyses both solutions were at 0°C. The standards contained measured equivalent amounts of silver and chloride, 9.3718 g. of potassium nitrate per 1520.7 g. of solution, and were 0.3025 molar in nitric acid. Seven of these solutions were made up to cover the range of silver and chloride concentrations from 0.590 to 0.610 mg. (as silver) per liter. To make standard solutions 8 and 9 two 14-g. samples of silver chloride from completed analyses were rinsed and brought to equilibrium with solutions made up without chloride or silver to the same concentration as the other standards, from two different samples of potassium nitrate and nitric acid.

After preliminary analyses the supernatant analytical liquid was adjusted more closely to the end-point, the additions of chloride or silver being corrected to the original volume in the usual manner. The chloride and silver concentrations of the solution were finally determined by at least three nephelometric and three potentiometric analyses made over a period of at least five days with three different standard solutions. The analytical system was shaken once only after each set of withdrawals.

Measurements of the solubility of silver chloride in the analytical and standard solutions permitted an improvement in the manner of determining the chloride concentration from the potentiometric analyses. These measurements are summarized in table 1. The data show that the chloride concentration may be calculated precisely from the expression: $[\mathrm{Cl}] = 0.3697/[\mathrm{Ag}]$ or the corresponding approximation: $[\mathrm{Cl}] = 1.216 - [\mathrm{Ag}]$. The silver concentration was calculated from the E. M. F. of the cell Ag | analytical solution | standard solution | Ag by the expression: $\log [\mathrm{Ag}] = \pm E/0.0542 + \log S$, where S is the silver concentration of the standard solution. All concentrations are expressed in milligrams of silver per liter, and E is in volts. The data obtained from the corresponding cell with silver chloride electrodes were used only in analysis 3, but furnished valuable confirmatory information in the other analyses.

Equal-opalescence tests made in the usual manner, in connection with the standard solution analyses of various systems in equilibrium at 0°C., gave further evidence that there is an essential difference in the stability of the sols precipitated with excess silver and excess chloride upon which various factors may operate to produce marked differences in color and opalescence. Comparison of the equal-opalescence ratios with the accurately determined values of the silver and chloride concentrations showed that any estimate of the KCl:Ag ratio based on the assumption that the unit equal-opalescence ratio is characteristic of solutions at the correct

TABLE 1

Solubility of silver chloride at 0°C.

NO. OF ANALYSES	TYPE OF ANALYSIS	SOLUTIONS ANALYZED	QUANTITY MEASURED	AVERAGE MG. OF Ag PER LITER
90	Nephelometric	15 Analytical	$\sqrt{[Ag]\cdot[Cl]}$	0.608
6	Nephelometric	Standard No. 8	[Ag] and [Cl]	0.608
6	Nephelometric	Standard No. 9	[Ag] and [Cl]	0.607
3	Potentiometric	Standard No. 8	[Ag] only	0.609
3	Potentiometric	Standard No. 9	[Ag] only	0.608

TABLE 2

Summary of end-point determinations

NO	INITIAL VOLUME IN LITERS	Ag ADDED IN SOLN TOTAL MG	NEPHELOMETRIC ANALYSES MG OF Ag PER LITER AS		POTENTIOMETRIC ANALYSES MG OF Ag PER LITER AS		AVERAGE EXCESS Ag MG PER LITER
			Chloride*	Silver	Chloride*	Silver	
1	1.56	−0.795	0.56	0.66	0.54	0.68	+0.12
		−1.057	0.612	0.600	0.621	0.595	−0.019
2	1.57	−0.704	0.605	0.616	0.584	0.632	+0.030
3	1.56	−0.748	0.628	0.613	0.626	0.590	−0.026
4	1.57	−0.475	0.56	0.64	0.57	0.64	+0.08
		−0.689	0.604	0.610	0.604	0.612	+0.007
5	1.57	−0.683	0.618	0.599	0.613	0.603	−0.015
6	1.57	−0.628	0.57	0.64	0.55	0.67	+0.10
		−0.729	0.59	0.61	0.60	0.61	+0.02
		−0.786	0.629	0.595	0.624	0.592	−0.033
7	1.57	−0.594			0.57	0.64	+0.07
		−0.712	0.61	0.61	0.604	0.612	+0.004
8	1.58	−0.733	0.605	0.615	0.608	0.608	+0.005
9	1.57	−0.208	0.603	0.606	0.598	0.618	+0.012
10	1.59	−0.307	0.605	0.611	0.597	0.619	+0.014
11	1.57	−0.208	0.602	0.595	0.623	0.593	−0.018
12	1.57	−0.139	0.62	0.59	0.63	0.58	−0.04
		−0.085	0.598	0.611	0.596	0.620	+0.019
13	1.56	0.000	0.603	0.606	0.608	0.608	+0.002
		−0.056	0.622	0.592	0.633	0.583	−0.040
14	1.59	0.000	0.625	0.601	0.632	0.584	−0.036
15	1.57	0.000	0.605	0.601			−0.004

* The values in this column are chloride concentrations in milligrams per liter, multiplied by the factor Ag/Cl.

end-point would be subject to corrections which would vary with the temperature, the acid concentration and volume of the analytical solutions, the size of the analytical samples, and the method of forming the test suspensions. Equal-opalescence tests made upon solutions containing equivalent amounts of silver and chloride and saturated at 25°C. gave approximately unit ratios, but were insensitive to additions of excess silver nitrate or potassium chloride equivalent to 0.20 mg. of silver per liter.

DISCUSSION OF RESULTS

The amounts of silver "subtracted" from the analytical solutions and the results of the standard solution analyses made at the corresponding stages

TABLE 3

Summary of analyses

NO.	KCl NO	Ag NO.	KCl IN VACUUM	Ag IN VACUUM	TOTAL Ag ≎ KCl	RATIO KCl:Ag
			grams	*grams*	*grams*	
4	1	1	7.174405	10.381709	10.38101	0.691109
15	2	1	7.159125	10.358857	10.35886	0.691111
6	3	1	7.139503	10.331248	10.33051	0.691108
7	4	1	7.110874	10.289814	10.28910	0.691107
3	5	1	7.119655	10.302444	10.30174	0.691112
13	1	2	7.113533	10.292932	10.29294	0.691108
9	2	2	7.124221	10.308618	10.30839	0.691109
10	3	2	7.241729	10.478735	10.47841	0.691110
12	4	2	7.128585	10.314855	10.31474	0.691107
2	5	2	7.163709	10.366249	10.36550	0.691111
5	1	3	7.132066	10.320468	10.31981	0.691104
11	2	3	7.151197	10.347646	10.34747	0.691106
14	3	3	7.230660	10.462442	10.46250	0.691103
8	4	3	7.212326	10.436676	10.43594	0.691105
1	5	3	7.102363	10.277835	10.27681	0.691106
Average						0.691108
Probable error						±0.0000005

of adjustment to the end-point are given in table 2. From these data and the original weights of silver and potassium chloride added (table 3) the KCl:Ag ratio may be calculated. In table 3 the results of calculations based on the final sets of analyses are summarized. No corrections have been applied for hydrogen in the silver or nitrogen in the fused salt; they could hardly affect the final average by more than a few parts per million.

While the analytical procedures were designed to reduce to a minimum all of the errors in the determination of the ratio, the plan of the research was calculated to reveal any sources of error in the procedures. The only factor whose effect upon the accuracy of the procedures could not be estimated in two different ways was the composition of the precipitated silver chloride. However, satisfactory evidence that silver chloride is a compound with an accurately reproducible composition was obtained in work on the atomic mass of sodium (2). The absence of effects due to greatly changed conditions of precipitation in five of the present determinations offered further evidence that silver chloride formed under the conditions of these experiments has a definite composition not measurably altered by adsorption effects.

The agreement of the independent and basically different nephelometric and potentiometric analyses of the solutions obtained by the analytical reaction and by the reverse method of synthesis (table 1) offers proof of the soundness of the end-point. The absence of variations in the final results shows the adequacy of the purifications and the precision of the method as a whole.

The fifteen determinations of the ratio have been made with sufficient independence to give general validity to the final average. It may thus be concluded that the value 0.691108 ±0.0000005 represents an accurate estimate of the KCl:Ag ratio. This value agrees well with the average of Stas's four series of determinations and is reassuringly close to the mean of the various results which have been obtained in recent times with the equal-opalescence method. The corresponding value of 39.100 for the atomic mass of potassium (Ag = 107.880; Cl = 35.457) is also close to the mean obtained in determinations of this constant through other ratios.

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HYDROLYSIS OF ALKALI CHLORIDES

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The work described herein offers information regarding the purity with which sodium chloride and potassium chloride may be obtained in weighable form. It also shows the extent to which samples of the latter material taken from different sources and purified by different methods may be depended upon to have the same composition. The experiments were undertaken primarily to supplement researches on the atomic masses of sodium and potassium, but they have a more general interest because of the many cases in which the alkali chlorides are used as reference standards in analytical and physical chemistry. The findings thus have a bearing on the preparation and handling of the compounds in conductance measurements, E. M. F. measurements, reaction velocity measurements, pH measurements, and other work in which weakly buffered solutions of the salts are used. Moreover, the method employed in the tests is a general one, applicable in the preparation of other compounds in weighable form of known composition.

By crystallization in platinum dishes sodium chloride and potassium chloride may be obtained free from all weighable impurities except water, platinum, and atmospheric gases. The platinum impurities are easily kept to negligible amounts, and the water and gases may be removed by fusion of the salts, but there is a limit set upon the purity of the fused material by the slight hydrolysis which occurs during fusion. The experiments supply quantitative evidence upon the magnitude of this limit when the pure well-dried salts are fused either in air of known humidity or in dry nitrogen.

REAGENTS

The potassium chloride, water, and nitrogen used in this work were prepared as set forth in the preceding article. The sodium chloride was taken from one 25-g. and two 26-g. fractions from a single source, the purification of which is described elsewhere (2).

EXPERIMENTAL

The experiments consisted in fusing portions of the salt samples under various conditions and determining the alkali in the fused material. In one set of experiments the gases evolved during the heating and fusion process were analyzed for acid, chloride, and total electrolyte. In this case the salts were fused in a 15-cc. platinum–rhodium boat in a closed platinum-lined quartz muffle (3), in a current of nitrogen. The gases from the muffle passed through a 200-cm. coil of dry 5-mm. Pyrex tubing into a conductance cell under conditions such that the absorption of electrolytes was practically 100 per cent complete.

The salts were weighed before and after fusion; the observed difference in weight includes loss by volatilization, loss of water, and mechanical loss. The platinum–rhodium boat lost about 0.01 mg. in each fusion; with pure platinum the losses were from 0.03 mg. to 0.06 mg. per fusion. The main part of these platinum losses did not take place from the salt–platinum system until the salt was dissolved out of the boat, i.e., the loss by volatilization of platinum was a minor effect.

The fused, partially cooled salts were transparent, colorless, and free from bubbles when removed from the muffle, but sometimes cracked on further cooling.

For each experiment 50 cc. of distilled water was placed in the cell and the conductance was determined after a slow current of nitrogen had removed most of the carbon dioxide. With the nitrogen still passing, the temperature of the furnace was gradually raised as follows: 3 amperes, 2 hours; 4 amperes, 30 minutes; 5 amperes, 30 minutes; 6 amperes, 10 to 15 minutes. The current was then raised to 7.7 amperes (8.1 amperes for the sodium chloride), whereupon the salt fused in about fifteen minutes. The current was shut off two to ten minutes after the salt had fused. In experiments 1 to 3 the nitrogen was passed continuously; in experiment 4 the gas current was stopped after the salt had fused; in experiments 5 to 12 it was stopped when the current was raised from 6 amperes; the furnace gases were passed into the conductance cell after the salt had ceased to volatilize.

Conductance measurements were made during the heating process and after the absorption of electrolytes was complete. The measurements were made at temperatures from 22°C. to 26°C. and have been corrected accordingly in calculating the electrolyte concentration, which is expressed arbitrarily as HCl.

Following the conductance measurements, two 10-cc. portions of solution from the cell were analyzed for acid (H^+) by titration with 0.001 *M* alkali in a nitrogen atmosphere. Another 20-cc. portion was analyzed nephelometrically for chloride by comparison with standard potassium chloride solutions.

In some cases the alkali content of the fused salt was determined by titration with 0.001 *M* nitric acid and methyl red indicator in the carbon dioxide-free atmosphere and solutions obtainable with cells of the type used by Kolthoff and Kameda (4). Freshly prepared solutions made from water, indicator, and the recrystallized neutral salts furnished the reference end-point. For the samples which were used in atomic weight analyses,

TABLE 1

Hydrolysis of salts fused in dry nitrogen

SALT	NO	SAMPLE WEIGHT	LOSS ON FUSION	SPECIFIC CONDUCTIVITY × 10^6		TOTAL MOLES × 10^6 FROM				NITROGEN
				Initial	Final	Evolved gases			Salt	
						HCl	Cl	H^+	OH^-	
		grams	*mg*							*cc per minute*
KCl	4	7 1		0 47	8 93$^{22\circ}$	1 14	1 0	<1	0 05	18
KCl	2a	7 1		0 60	6 78$^{23\circ}$	0 75	0 42	<0 3		10
KCl	2b*	7 1	2 8	0 36	9 99$^{22\circ}$	1 19	1 4	<1	<0 02	25
KCl	3	7 2	3 5	0 58	4 28$^{26\circ}$	0 43	0 44	0 2	<0 02	45
KCl	2	7 2	3 6	0 38	0 98$^{25\circ}$	0 07	0 12	0 15	<0 05	32
KCl	4	7 1	7 5	0 31	5 32$^{24\circ}$	0 60	0 56	0 7	<0 09	27
KCl	1	7 1	9 0	0 31	2 16$^{23\circ}$	0 22	0 24	0 3	<0 08	37
KCl	3	7 2	4 8	0 33	0 70$^{25\circ}$	0 04	0 06	0 14	−0 09†	30
KCl	2	7 2	4 6	0 28	1 04$^{24\circ}$	0 09	0 09	<0 09	<0 09	35
KCl	5	6 9	3 8	0 63	0 84$^{22\circ}$	0 03	0 12	<0 05	−0 11†	30
NaCl	2	7 4	8 9	0 44	1 09$^{25\circ}$	0 08	0 10	<0 05	0 29	40
NaCl	4	6 6	10 5	0 61	2 36$^{26\circ}$	0 20	0 39	0 1	0 24	35

* Second fusion of same material

† Solution of fused salt more acid than reference solution.

TABLE 2

Hydrolysis of salts fused in moist air

SALT	NO	SAMPLE WEIGHT	LOSS ON FUSION	RELATIVE HUMIDITY	MOLES × 10^6 (AS OH$^-$)
		grams	*mg*		
*NaCl	2 and 4	6 5	8 6	68	5 6
NaCl	1	6 3	13 3	67	5 8
*KCl	5	7 2	6 1	70	0 24
KCl	5	5 7	6 8	77	0 13
KCl	4	6 8	6 6	72	0 35
KCl	3	4 4	4 9	58	0 20
KCl	2	4 9	5 0	49	0 19
KCl	1	6 0	4 6	63	0 17

* Fused in 20-cc. crucible in porcelain beaker.

the alkali was estimated by the method of Hönigschmid (1), using 50-cc. volumes of solution, 0.05-cc. portions of 0.004 *M* methyl red solution, and 0.001 *M* nitric acid. Microburettes were used throughout.

The results of the above-described experiments are summarized in table 1.

A second set of tests was made in which the salts were fused under exactly the same conditions as before, except that the cap of the muffle was removed and no nitrogen was passed. These experiments are summarized in table 2.

The muffle was washed out at intervals during the fusions. Table 3 gives the results of analyses made for alkali in the washings.

TABLE 3

Alkali recovered from muffle

SALT FUSED	TOTAL IN GRAMS	NO. OF FUSIONS	MUFFLE CAP	MOLES × 10^6 (AS OH^-)
KCl	84	11	On	1 0
KCl	57	8	On	<0 9
NaCl	14	2	On	1 08
NaCl	6	1	Off	
KCl	28	5	Off	0 76

TABLE 4

Observed mass of salts exposed to moist air

SALT	NO	TIME EXPOSED	RELATIVE HUMIDITY	MASS IN GRAMS	SALT	NO.	TIME EXPOSED	RELATIVE HUMIDITY	MASS IN GRAMS
KCl	5	10 min.	8	7.102363	NaCl	2	9 A.M.	65	5.470888
		7 hrs.		7.102360					5.470906
							to		5 470908
KCl	4	10 min.	20	7.110874					5 470906
		8 hrs.		7.110863			2 P.M.		5 470899
KCl	3	10 min.	51	7 230660	NaCl	2	30 min.	85	Not found
		5 hrs.		7.230663					
KCl	2	10 min.	54	7 159125					
		15 hrs.	36	7 159124					

Tests were made to determine if the salts fused in nitrogen take up moisture when exposed to air during weighing. The salts were weighed without removing them from the boats or crucibles. The data obtained are summarized in table 4.

Eight of the identical fused potassium chloride samples listed in table 1 were used in the atomic mass determination described in the foregoing paper. Parts of the three sodium chloride fractions used in another atomic mass determination (2) gave values for the NaCl:Ag ratio from 0.541812 to 0.541821.

DISCUSSION OF RESULTS

The total loss of hydrogen chloride due to hydrolysis was extremely small when the salts were fused in dry nitrogen, but the amount of alkali left in the salt in the boat was even smaller. The larger part of the hydrolysis occurred either in the vapor phase or at the walls of the muffle.

When the nitrogen was passed continuously during the heating and fusion, the high values obtained from the conductance data were due to volatilized salt. The conductance measurements made at intervals as the temperature was raised showed that the hydrolysis took place mainly after the current was raised from 6 amperes.

Sodium chloride has a much greater tendency to hydrolyze than potassium chloride when fused in moist air. The corresponding difference observed for the samples fused in nitrogen is not significant, for the 107 g. of material from which the sodium chloride fractions were taken was cut from a 168 g. quantity which yielded 0.0011 g. of sodium bicarbonate to the rejected mother liquors.

SUMMARY

It has been shown that carefully purified sodium chloride and potassium chloride consistently hold less than one or two parts per million of alkali when fused in dry nitrogen under a specified set of conditions. It may be inferred that samples of the salts taken from different sources and purified by different methods may be prepared constant in composition to the same extent. The latter conclusion has been confirmed to the limit of the experimental precision, and independently, by analysis of various samples of the salts.

Sodium chloride and potassium chloride prepared, purified, and fused as described may be weighed in air of low and moderate humidity without taking up weighable amounts of moisture.

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THE STORAGE OF POLONIUM SOLUTIONS

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Polonium has been used but little as a radioactive indicator because, except in strong acid solution, it appears to be colloidally dispersed (18, 19). This behavior is unfortunate, because the radioelement possesses ideal properties which qualify it for use as an indicator. Polonium is a strong alpha-radiator, and therefore produces an intense and easily measurable ionization. Because it is the last active member of the uranium–radium series, there is no need for multiple measurements or for delay until establishment of radioactive equilibrium with succeeding products. In addition, it is sufficiently long-lived to obviate the necessity of making decay corrections in most cases. Since polonium in true solution would constitute a valuable tool for a proposed study of crystalline precipitates, it was believed advisable to determine, if possible, useful conditions under which radiocolloid (23) formation by polonium is minimized.

Elements like polonium, radium E, thorium B, etc., under suitable conditions of acidity, behave as though they were colloids. This conclusion is drawn from their dialyzability (18, 19), the small velocity with which they diffuse in solution (19, 20, 22), their centrifugability (2, 4, 24) and settling under gravity (16), their behavior in an electric field (8, 9, 10, 15, 19), and from the fact that radiograms (1, 11) of small quantities of their solutions apparently show the presence of large aggregates of radioactive atoms. Because it is uncertain whether true colloids are involved, the term "radiocolloid" (23) was coined.

Opinions as to the cause of the phenomenon are not in accord. One explanation (19) views the effect as true colloid formation, the sol consisting of extremely insoluble products of the hydrolysis of salts of radioelements. Actually, those radioactive elements which would be expected to yield, upon hydrolysis, insoluble hydroxides and basic salts, do show a pronounced radiocolloid effect (11). Since the solubility products of these compounds of lead and bismuth are never exceeded in solutions containing only the radioactive isotopes of these common elements, it is difficult to see how such precipitates can be formed. Hence others (15, 24, 26) hold that the phenomenon is really a pseudo-colloid formation resulting from the adsorption of radioelements by traces of colloidal impurities, such as dust, alumina, and silica particles, suspended in the liquid media employed. This view is supported by the fact that it is almost impossible to prepare and store in the laboratory, water which is truly optically void (13, 25).

Since the chief source of suspended silica is the walls of glass containers used for storage purposes, it occurred to the authors to study the behavior of polonium solutions kept in paraffined bottles. This procedure has the additional advantage of preventing adsorption of the polonium by the glass (5, 21) itself. Though by this simple expedient the radiocolloid effect could not be avoided entirely, it was found that polonium could be maintained in dilute acid solutions stored in paraffin for periods of time sufficiently convenient to permit its use as an indicator. The necessity of preparing fresh stock solutions for each set of experiments was thus eliminated.

EXPERIMENTAL

The centrifuging method (12) of demonstrating radiocolloid formation, was used in these experiments. Paraffined, cylindrical copper cups (2.5 cm. in diameter × 7 cm. in height), closed by paraffined stoppers, were used for centrifugation. Into each cup was placed 16 ml. of a given polonium solution, and the whole rotated for various times at a speed of 3000 R.P.M., with a radius of 22 cm. Then three 2.63-ml. samples of the supernatant liquid were carefully sucked off and evaporated in matched watch-glasses on a water bath, prior to measurement in a Lind electroscope (17) equipped with an open door chamber. Samples of the uncentrifuged solution were taken as standards for comparison. All pipets used were paraffined. All experiments were done in duplicate. Electroscopic measurements were accurate to within ±1 per cent. In most cases, centrifuging was carried on for an hour.

Polonium was obtained from a number of old radon bulbs, after digesting the crushed glass in acid, by currentless electrochemical deposition (5, 6, 7) on silver. The silver was dissolved in concentrated nitric acid, hydrochloric acid was added to precipitate the silver, and, after removal of silver chloride by filtration, the filtrate was evaporated to dryness in a Pyrex beaker on a water bath. The polonium source, from which all other solutions were subsequently prepared, was obtained by taking up the residue in cold 1.015 *N* nitric acid. Boiling the acid solution to accelerate solution was found to yield a large amount of centrifugable polonium, and was therefore undesirable. In this fashion, 125 ml. of a stock solution containing 100 E.S.U. of polonium was prepared and stored in a paraffined bottle. The solutions used in the centrifuging experiments were formed by diluting this source with twice-distilled water, and then stored in large paraffined containers. This water was used shortly after the second distillation, to avoid long standing in glass receivers. More active solutions were made by evaporating a portion of the source, and taking up the residue in a solution of the proper acid concentration. The centrifugability of the polonium was measured at various times after the preparation of solutions. Results are expressed as per cent of polonium left in solution after centrifugation. Approximate polonium quantities are given in electrostatic units.

RESULTS

The acid concentration and polonium content of solutions studied, as well as the results of centrifugation experiments, are summarized in table 1.

TABLE 1

Centrifuging of polonium solutions

SOLUTION	COMPOSITION		AGE OF SOLUTION	DURATION OF CENTRIFUGING	POLONIUM LEFT
	Nitric acid concentration	Polonium content E.S.U./16.1 ml.			
	N		*days*	*hours*	*per cent*
1	1.09	0.06	45	1	98.8
2	0.114	0.06	45	1	97.3
3	0.0196	0.07	10	3	98.0
	0.0196	0.07	13	2	98.2
4	0.0108	0.48	22	1	95.2
5	0.00534	0.07	7	0.5	100
	0.00534	0.07	7	1	100
	0.00534	0.07	7	3	100
	0.00534	0.07	12	1	99.4
	0.00534	0.07	39	1	99.8
	0.00534	0.07	45	1	98.2
6	0.00534	0.59	9	1	96.2
7	0.00059	0.08	11	1	96.5
	0.00059	0.08	11	2	97.9
8	0.00059	0.80	8	1	96.3

From these data, it is evident that polonium solutions can remain practically uncentrifugable for long periods of time. Even the 0.00059 *N* acid solution shows little indication of radiocolloid formation after a week of standing. This is especially significant, because A. Korvezee (14) has recently reported a region of maximum centrifugability near this acid concentration.

That this is an improvement over storage in uncoated glass vessels can be illustrated simply by following the behavior of solution 5 kept in a common glass container for six days. After this period, the activities of the centrifuged and uncentrifuged solutions were measured in the usual fashion. By comparing these electroscope discharges with samples of the original solution kept in paraffin, both adsorption by glass walls and radiocolloid formation could be determined. Using 200 ml. in 250-ml. bottles, it was found that 8.4 per cent of the polonium had been removed from solution by the glass walls, and of the polonium remaining in solution, 20 per cent was removed by centrifuging for one hour. It seems definite that glass containers are undesirable as stock bottles for polonium solutions.

The disadvantage in using glass is further illustrated by preparing radioactive solutions with the use of inactive acid solutions which had been shaken gently for several days in common glass bottles. A 0.00059 *N* nitric acid solution was employed for this purpose. After the dilute acid had been transferred to paraffined flasks, portions were centrifuged for an hour and a half, and half of the supernatant liquid separated from the remaining liquid. Then three polonium solutions were made by diluting fresh solution 8 with measured volumes of uncentrifuged acid, the supernatant liquid, and the residual liquid. These solutions were shaken in paraffin for two days, and centrifuged for one hour in the usual manner. Table 2 shows the results of these experiments.

TABLE 2

Radiocolloid formation in solutions prepared from glass-stored acid

ACID SOLUTION EMPLOYED	COMPOSITION		AGE OF SOLUTION	POLONIUM LEFT
	HNO_3 concentration	Polonium content E.S.U / 16.1 ml.		
	N		*days*	*per cent*
Uncentrifuged acid	0.00059	0.077	2	81.9
	0.00059	0.077	8	72.5
Supernatant liquid	0.00059	0.18	2	93.0
Residual liquid	0.00059	0.11	2	39.5

The "uncentrifuged acid" solution clearly shows the radiocolloid formation, accompanied by its characteristic increasing centrifugability with age (3). On the other hand, the "supernatant acid" solution is practically free from the disturbing phenomenon. In accord with the last observation is the fact that the "residual acid" solution shows the greatest loss on centrifuging. Apparently the dilute acid, during its contact with glass, had become contaminated with impurities which promote the centrifugability of polonium.

DISCUSSION

Objections might be directed toward the use of such small amounts (0.06 to 0.8 E.S.U.) of polonium in studying the radiocolloid effect. These are unfounded, because the above experiments unquestionably point to the loss of polonium on centrifuging our weak solutions, unless paraffined containers are used. Furthermore C. Chamié and M. Haïssinsky (3) have demonstrated the phenomenon using 0.05 E.S.U. The stability of our solutions can be explained best by the care taken to avoid contact with uncoated glass walls. Even this precaution is insufficient to eliminate the effect in 0.00059 *N* acid after two weeks of storage.

Experiments of this type unfortunately are chiefly empirical, and do not explain the mechanism of radiocolloid formation. Probably glass alone is not responsible. Dust particles too will produce the effect, as was shown by I. E. Starik (21). We have found that as little as 25 mg. of laboratory dust, shaken in 16 ml. of solution 5 for ten minutes, will cause a separation of 87 per cent of the polonium after centrifuging for only ten minutes at 1600 R.P.M. This, together with colloid-producing impurities in the nitric acid used, probably accounts for the small losses found in table 1.

SUMMARY

1. The use of glass vessels for the storage of polonium solutions is undesirable.
2. Coating storage containers with paraffin eliminates, to a considerable extent, the disturbing radiocolloid effect in polonium solutions.
3. Polonium solutions which are as dilute as 0.00059 *N* in nitric acid may be used for more than a week if stored in paraffined vessels. More concentrated acid solutions may be kept for longer than a month and a half.

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THE THERMAL DECOMPOSITION OF DIETHYLAMINE[1]

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The study of the kinetics and mechanism of the decomposition of diethylamine was undertaken in order to continue the work in the amine series under investigation in this laboratory. The decompositions of the primary amines appeared at first sight to offer simple examples of homogeneous unimolecular reactions (8, 9, 11). This simplicity, however, was shown by Taylor (10) to be illusory in the decomposition of dimethylamine, owing to a mutual compensation of several concurrent reactions. It was hoped therefore that a fuller investigation, particularly of the mechanism, might yield a possible scheme of analysis of the complete results.

In a study of the catalytic influence of iodine on amines, Bairstow and Hinshelwood (1) assume the over-all change occurring with diethylamine to be

$$(C_2H_5)_2NH \rightarrow C_2H_6 + CH_4 + HCN$$

despite the fact that in the uncatalyzed reaction only from 15 to 30 per cent of the theoretical amount of hydrogen cyanide could be detected with silver nitrate and that this fell to from 5 to 10 per cent in the iodine-catalyzed decomposition. They conclude that the reaction is initially homogeneous and unimolecular. In view of the fact, as will be shown, that methane and nitrogen are the chief products and that no hydrogen cyanide was detected in any stage of the reaction, although a hydrazine which readily reacted with silver nitrate was always found, this mechanism appears untenable. Furthermore, there appears a distinct possibility that hydrogen cyanide, if formed, would add on to any unchanged amine and thus reduce still further the observed rate of pressure increase.

The rate of decomposition was studied statically in an apparatus identical with that used in the previous work already published. The diethylamine used was an Eastman sample, redistilled over lime, and boiling from 55.5 to 56.0°C. The capillaries connecting the amine reservoir, reaction vessel, and manometer were maintained at 60°C. to prevent any condensation occurring. Data were obtained over the temperature range from 510 to 540°C., and at pressures from 40 to 400 mm. The pressure increase during reaction averaged around 160 per cent, although a perceptible effect of both temperature and pressure was observable. Thus at 510°C. the pressure increase varied from 182 to 166 per cent at pressures ranging from 44 to 419 mm., whilst at 540°C. the variation was from 176 to 134 per cent over the same pressure range. Such variations, however, may not be a true indication of the existence of an equilibrium but may be merely due to the fact that the end points taken are fictitious, owing to very slowly occurring secondary reactions.

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[1] Abstract from a thesis presented by C. R. Herman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

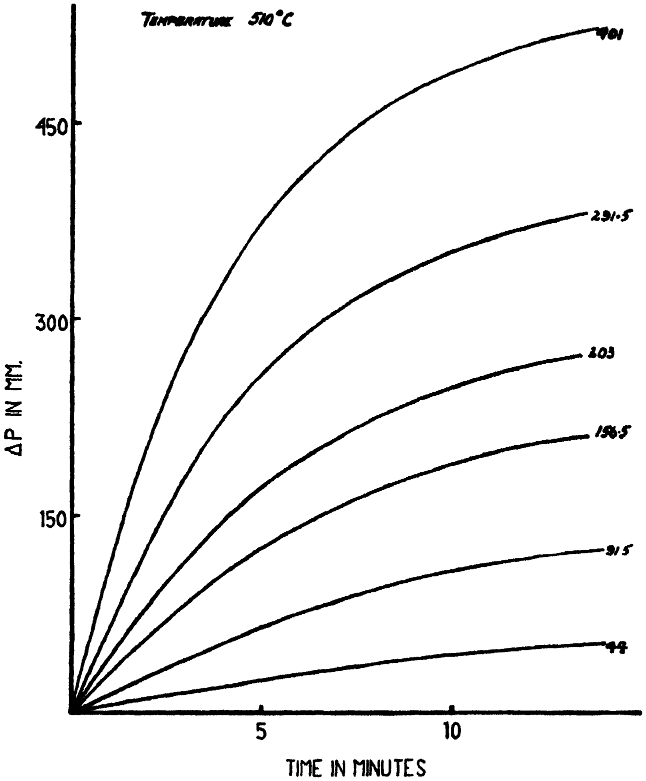

FIG. 1. THERMAL DECOMPOSITION OF DIETHYLAMINE

A typical diagram of the rate of pressure change with time is shown in figure 1 for initial pressures of 44, 91.5, 156.5, 203, 291.5, and 401 mm. at 510°C. Similar curves were obtained at the other temperatures.

In table 1 are given the values of the quarter-lives for the various temperatures and pressures studied, calculated as the time necessary for one quarter of the total pressure increase to occur.

The only obvious conclusion one can draw from these values is that the reaction has an order lying between one and two, more closely approaching the former however, but being in all probability complex. The variation in quarter-life with pressure is the more marked the lower the pressure, and the possibility therefore remains that at higher pressures a constant life might be found.

The reaction was shown to be homogeneous under the conditions studied by increasing the surface to volume ratio of the reaction vessel eleven times by packing with short lengths of Pyrex tubing. Table 2 shows a comparison of the actual pressure readings at various times for the same initial pressure in the packed and unpacked vessels.

TABLE 1

Values of the quarter-lives at different temperatures and pressures

INITIAL PRESSURE	*t* IN MINUTES	INITIAL PRESSURE	*t* IN MINUTES
Temperature = 510°C.		Temperature = 530°C.	
44.0	3.80	43	1.45
58.5	3.35	71	1.34
81.0	3.05	88	1.15
91.5	2.80	134	1.09
156.5	2.23	188	0.92
203	2.08	228	0.88
257.5	1.96	256	0.83
291.5	1.87	295	0.76
322.5	1.74	342	0.74
374.5	1.66	368	0.74
401.0	1.56	410	0.70
419.0	1.50	452	0.69
Temperature = 520°C.		Temperature = 540°C.	
37	2.30	41	1.20
85	1.87	91	0.85
127	1.65	129	0.77
142	1.48	152	0.68
185	1.35	209	0.63
204	1.30	252	0.60
245	1.21	275	0.57
282	1.15	315	0.56
385	1.03	358	0.54
432	0.96	439	0.50

The data in table 2 show that the reaction is in the main homogeneous, though there are indications of a speeding up over the later portion of the reaction, though the pressure increase for the unpacked vessel was 174 per cent whilst that for the packed vessel was 175 per cent.

The effects of added nitrogen, hydrogen, and ammonia were studied at the highest and lowest temperatures, namely, 540 and 510°C., and at initial pressures of amine of 40 and 200 mm., the pressure of added gas being 150 mm. These data are presented in table 3 in the form of percentage total pressure increase and the quarter-life.

It is readily seen that the effect of nitrogen is negligibly small at all temperatures and pressures. Ammonia, however, appears to retard the rate of pressure increase, and in all probability does so by specific chemical reaction. The effect of hydrogen is very marked. In the first place the end point is considerably reduced, showing again a probable chemical action. The quarter-life based on this end point is also largely reduced though, owing to the disproportionate end points, the effect is apparently larger than it actually is for the earlier portions of reaction. The actual pressure change for equivalent times is not however as great for the amine in presence of hydrogen as in its absence. There appears then to be an actual retardation by hydrogen.

TABLE 2

Changes in pressure observed when the reaction occurs in packed and in unpacked vessels

Temperature = 510°C.

TIME	PRESSURE CHANGE	
	Unpacked vessel. Initial pressure 233 mm.	Packed vessel. Initial pressure 230 mm
minutes		
0 5	26	25
1.0	51	50
2 0	99	94
3.0	139	134
4 0	170	168
5 0	200	195
6 0	223	220
7 0	242	240
8 0	258	255
10.0	283	283
12 0	302	303
14 0	316	319
16 0	326	332

With the view of determining the end products of reaction a weighed amount of amine was sealed in a glass bomb and heated for three days at 500°C. to render reaction complete. The gaseous products were then analyzed,[2] yielding 2.1 per cent of ammonia as water-soluble, 3.2 per cent of unsaturated hydrocarbon absorbed by bromine, 0.2 per cent of hydrogen by preferential combustion over copper oxide, 70.1 per cent of methane, and 2.3 per cent of ethane. The remaining 23 per cent is nitrogen. The reaction in the main then appears to yield methane and nitrogen in the ratio of three to one. The difference between this value and their ratio in the original amine is to be accounted for by the large amount of black deposit obtained in such bomb experiments. Such results, though of little use in determining a mechanism, are necessary to the elucidation of the final goal of the reaction.

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[2] Thanks are due to H. Tarnpoll of this laboratory for the gas analyses.

To obtain the details of the mechanism of the reaction in its earliest stages a small amount of liquid diethylamine was sealed in a tube and maintained at only 200°C. for twenty-four hours. Upon opening, a small pressure increase was noted, pointing to the accumulation of gaseous products. In other cases at 400°C. and for periods varying from one to eighteen hours similar gaseous products were found and analyzed. In no case was hydrogen found in other than mere traces. Nitrogen was always present. From the ratio of the carbon dioxide to the water formed on combustion the gas appeared to be a mixture of methane and butane. To test this specifically, a sample of the gas was kept in a solid carbon dioxide bath for some time, during which a decrease in volume was observed. The remaining uncondensed gas on combustion proved to be practically

TABLE 3

The effect of added gases

PRESSURE OF AMINE	GAS	PRESSURE OF GAS	PER CENT INCREASE	*t*
Temperature = 510°C.				
mm.		*mm.*		*minutes*
44			182	3.80
40	NH_3	153.5	179	4.20
43	N_2	151	182	3.75
46	H_2	152	170	3.55
203			175	2.08
201	NH_3	153	171	2.20
210	N_2	152	174	2.17
180	H_2	155	157	2.10
Temperature = 540°C.				
41			176	1.20
41	NH_3	154	177	1.30
48	N_2	148	175	1.17
38	H_2	151	166	1.10
210			156	0.63
207	NH_3	154	164	0.66
212	N_2	153	156	0.65
225	H_2	158	139	0.57

pure methane. The condensed portion upon vaporizing and combustion analyzed as more nearly pure butane. Analysis of the remaining liquid in these experiments showed a considerable amount of unchanged secondary amine with only traces of primary and tertiary amine. Specific tests for the cyanide group as, for example, by the Prussian blue test showed its complete absence. In like manner nitriles too were shown to be absent. Upon addition of silver nitrate a marked reduction occurred, yielding the characteristic silver mirror. It is probable that this reduction is caused by a hydrazine, and the initial reaction may tentatively be indicated as

$$2(C_2H_5)_2NH \rightarrow C_2H_5NH{-}NHC_2H_5 + C_4H_{10}$$

a bimolecular reaction involving no volume change. Subsequent reaction involving the liberation of nitrogen from the hydrazine and the decomposition of butane would account for the presence of nitrogen, methane, and ethane in the end products, the over-all volume increase, and for the observed slow secondary reactions yielding apparent equilibria in the final state. The absence of hydrogen in the high temperature bomb experiments is in line with the observations of rehydrogenation of unsaturated hydrocarbons in the butane decomposition (2, 3). The excess of methane over ethane is to be expected also because of decomposition of the ethane (4).

The decomposition, at least in its earlier stages, of butane, is admittedly a unimolecular reaction even if of a chain type (5), and it would appear reasonable from the complexity of the molecule that the diethylhydrazine would also decompose unimolecularly. This is under investigation in this laboratory at the present time. Assuming that this latter rate is faster than the observed rate of pressure increase of diethylamine itself, the rate actually being measured here would be that of the bimolecular split into butane and hydrazine, a reaction without a volume change, in terms of the volume increase of the unimolecular reactions. It does not seem advisable at present to speculate on these relative rates, but the observation that the rate of pressure increase found would indicate a reaction order between one and two is easily accounted for, other than by the assumption that it is due to a quasi-unimolecular reaction in the pressure range where the Maxwell-Boltzmann distribution of activated molecules is not maintained.

In view of the fact that all analyses of the reaction products, whether taken in the early stages or later on, show the presence of some primary amine, ammonia, and unsaturated hydrocarbon, the possibility is suggested of an initial split of the amine into ammonia and an unsaturated hydrocarbon. The quantities of the latter usually found are hardly more than traces, however. Such a rupture therefore must be much more difficult than the hydrazine formation and consequently occur only to a minor extent. The reverse reaction, between ammonia and the unsaturated hydrocarbon, will account for the repressing effect of the added ammonia previously mentioned, since in the butane decomposition some unsaturateds must certainly be formed, as may also be possible in the hydrazine decomposition. The effect of added hydrogen would be similar though more marked.

There remains one factor, following as a consequence of the suggested mechanism, to be discussed. If the major reaction is bimolecular and without a volume change, followed by unimolecular reactions, there should be expected a period of induction in the reaction. Depending on the relative rates this may be long or short. However, as was first pointed out by Schumacher and Wiig (7) in the case of ethylamine, the induction period only evidences itself on an extremely clean surface and at low initial pressures, and even then appears to show only very poor reproducibility. Under the present conditions the reproducibility is perfect even with an extended surface, though the argument might be advanced that the surfaces were all uniformly poisoned. Under such conditions it is legitimate nevertheless, to treat the reaction as homogeneous. There seems however no reason to doubt that if the decomposition of diethylamine were to be studied in a vessel which had been pumped out to less than 10^{-6} mm. for several days, an induction period would be observed, as is the frequent observation with ethylamine in this laboratory at present. Indications in this case seem to point however to the hydrazine formation reaction as the one which is so extremely sensitive to traces of foreign material.

An approximate idea of the energy of activation of the early reaction may be obtained from the observed quarter-lives. The average value yielded by the simple Arrhenius equation for the various pressures studied is 49,000 calories. This value, though somewhat higher than that found in a similar manner for the primary amines, namely 44,000 calories, is more nearly in agreement with the value of about 50,000 calories taken as indicative of the strength of the C—N bond by Rice and Johnson (6) from a study of the free radical formation by thermal decomposition.

SUMMARY

The rate of pressure increase in the diethylamine decomposition over a temperature range from 510 to 540°C. appears to indicate a homogeneous reaction with an energy of activation, in the early stages, of 49,000 calories. Analysis of intermediate products suggests the mechanism to involve the formation and subsequent decomposition of diethylhydrazine and butane.

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THE POLYMERIZATION AND HYDROGENATION OF ACETYLENE[1]

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The literature on the polymerization and hydrogenation of acetylene is voluminous (2), but practically all of it deals with the mechanism (3) and products (6) of reaction. The only work dealing in any detail with the kinetics of the reaction is due to Pease (8) and Schlaffer and Brunner (12). Pease concludes that the rate-determining process is the primary reaction involving two molecules of acetylene. No quantitative data on the velocity of the hydrogenation are available. It was deemed desirable therefore to study both reactions more thoroughly.

The majority of previous work has been carried out by the dynamic method and suffers consequently, for such a complex reaction, from definite uncertainties of the time of contact and the analysis of the products. Since Pease, by the dynamic method, has shown that the only reaction of importance in the early stages of the thermal treatment of acetylene is the polymerization, and since the static method is admirably fitted for a study under such conditions, particularly if a back extrapolation to zero time is advisable, the static method as used previously by Taylor and his coworkers (14) was adopted.

POLYMERIZATION

Acetylene was generated by dropping water on Baker's calcium carbide, the gas evolution being moderated by suspension of the carbide in alcohol. The gas was purified by passage through acid copper sulfate and dried over calcium chloride. Analysis by precipitation as copper acetylide gave, as a mean of several determinations, its purity as 98.7 per cent. As shown later, the only objectionable impurity in the acetylene is oxygen, and absorption in acetylene-saturated alkaline pyrogallol showed considerably less than 0.1 per cent of oxygen in the acetylene used.

It is repeatedly mentioned in the literature that acetylene decomposes more readily and smoothly in the presence of carbon formed in its pyrolysis. This became quickly appreciated during the work because of the difficulty of obtaining duplicate results if the reaction system was thoroughly cleaned after each experiment. It was found, however, that after one run had been completed, the reaction vessel was apparently seasoned in some manner, and subsequent experiments at a given temperature and pressure were almost ideally reproducible. A change in either of these factors, however, necessitated a new seasoning. After each run the apparatus was thoroughly evacuated for at least one hour with a mercury vapor pump backed by an oil pump. To illustrate this reproducibility, data are presented in table 1 of two runs, fortunately at exactly the same initial pressure, at 535°C., showing the rate of pressure decrease with time of 399 mm. of acetylene.

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[1] **Abstract from a thesis presented by Andrew van Hook in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.**

TABLE 1

Reproducibility of results after seasoning of the reaction vessel

Temperature, 535°C.; initial pressure, 399 mm. of C_2H_2

TIME	PRESSURE DECREASE		TIME	PRESSURE DECREASE	
	I	II		I	II
minutes	*mm*	*mm.*	*minutes*	*mm.*	*mm.*
0.5	42	42	6	204	205
1.0	79	80	8	219.5	220
1.5	108	110	10	230	230
2	130.5	131	20	253	252.5
3	160	161	30	261	260
4	179.5	181	120	272	272

TABLE 2

Constancy of percentage pressure decrease with acetylene alone

TEMPERATURE	END-POINT
°C.	
495	0.671 (Average of 26 observations)
515	0.687 (Average of 10 observations)
535	0.669 (Average of 6 observations)
Mean....	0.675

With acetylene alone the total percentage pressure decrease on completion of reaction was constant, independent of temperature and initial pressure. These facts are shown in table 2 as the ratios of the total pressure decrease to the initial pressure.

The end-point of the reactions occurring at temperatures from 495°C. to 535°C. may therefore be taken as approximately two-thirds. It is worth while to mention in this connection some observations made on a new reaction vessel which had not been seasoned. The first run is slower, as measured by the actual rate of pressure decrease, by an amount approximately equivalent to a 5°C. change in temperature. The end-point too is much lower, about 0.36 as against 0.66, and would seem to indicate the preference of the decomposition reaction on the clean surface and its progressive decrease with seasoning.

In order to test specifically the order of the polymerization reaction a comparison of the fractional lives for various initial pressures was made. As a result of the distillation of the liquid products formed during polymerization Pease (8) decided that the major reaction involved four molecules of acetylene, giving a tetrapolymer. This is not inconsistent with the end-points herein quoted, since admittedly these are composite of both polymerization and decomposition, despite the inherent suspicion of a trimer that the value of two-thirds would suggest. Assuming then with Pease the formation of the tetramer, the fractional life will be the time necessary for the pressure to fall by an amount $P/f - P/4f$, where P is the initial pressure of acetylene and $1/f$ the chosen fraction. In table 3 are listed the times necessary for $\frac{1}{10}$, $\frac{1}{4}$, and $\frac{1}{2}$ of the acetylene to react. The products of initial pressure and time are included as a test of the bimolecularity of the reaction. The velocity constants quoted are calculated from these times by the usual expression for a bimolecular reaction $k = 1/t \cdot x/a(a - x)$, the units used being seconds and atmospheres.

TABLE 3

Times necessary for one-tenth, one-fourth, and one-half of the acetylene to react

Temperature, 495°C.

INITIAL PRESSURE P	$t_{1/10}$	Pt	k	$t_{1/4}$	Pt	k	$t_{1/2}$	Pt	k
mm	*minutes*			*minutes*			*minutes*		
748	0 50	374	0 0037	1 25	935	0 0045	3 35	2510	0 0050
729	0 51	372	0 0038	1 27	925	0 0046	3 67	2675	0 0047
558 5	0 68	380	0 0037	1 71	955	0 0044	4 69	2620	0.0048
380	1 15	436	0 0032	3 0	1140	0 0037	8 3	3160	0 0049
365	1 18	430	0 0033	3 1	1160	0 0036	8 8	3210	0 0040
103 5	7 0	725	0 0020	19 5	2020	0 0021	59 0	6100	0 0021
100	7 3	729	0 0019	20 6	2060	0 0021	67 2	6700	0 0019
92 5	8 0	738	0 0019	22 0	2150	0 0020	70 0	6460	0 0020
79	10 6	835	0 0017	29 0	2280	0 0019	89 0	7010	0 0018
70 5	11 4	800	0 0018	30 5	2145	0 0020	91 0	6400	0 0020
42	24 9	1042	0 0014	72 5	3020	0 0014	212	8860	0 0014
29 5	38	1150	0 0012	136	4000	0 0011	410	12050	0 0011
24	57	1370	0 0010	215	5150	0 0008	500	12000	0 0011

The figures indicate that in the early stages the reaction is bimolecular but deviates as the reaction proceeds, and furthermore, that the deviation is greater the smaller the initial acetylene pressure. Similar data at the other temperatures studied show that as the temperature increases the effect of the disturbing factor, which is undoubtedly decomposition, also increases. The values of the velocity constant obtained above from the one-tenth life were verified by a back extrapolation to zero time. Thus, by plotting the observed values of the pressure change in unit time against the time and extrapolating to zero time, the limiting rate of pressure change is found at the very start of reaction, and dividing this by the square of the initial pressure gives the velocity constant of the reaction at its inception. These values were slightly less than those found from the one-tenth life and are used in the subsequent calculation.

Since higher pressures favor polymerization the velocity constant calculated above is found to approach a limiting value at pressures which are only slightly above those actually studied. It is justifiable then to estimate this limiting value by plotting the velocity constants against the reciprocal of the pressure and extrapolating to infinite pressure. By this means the value of the velocity constant for the earliest reaction and under the ideal conditions of infinite pressure is obtained. In table 4 the values so found at the temperatures studied are given. For comparison there are included in the table also the values available in the literature already cited. In general the values found are almost double those reported by Pease. This is undoubtedly due to the approximate nature of the calculation in Pease's work, using a dynamic method, and to the devices used above to extrapolate to zero time and infinite pressure. Indeed, as Pease found, the value of *k* is usually the greater for those runs in which the least hydrogen and methane are found, that is, in which the pyrolysis was least.

TABLE 4

Values of the velocity constant

TEMPERATURE	VELOCITY CONSTANT	WORKER
°C.		
420	0.005–0.008	Schlaffer and Brunner
495	0.0039	Taylor and van Hook
500	0.0011–0.0015	Pease
515	0.0078	Taylor and van Hook
525	0.0030–0.0045	Pease
535	0.0145	Taylor and van Hook
550	0.0049–0.011	Pease

With the above values of the velocity constant an estimate of the energy of activation of polymerization can be obtained, using the simple Arrhenius equation. For the temperature interval 495°C. to 515°C. the value calculated is 41,700 calories; for the interval 515°C. to 535°C., it is 39,300 calories, giving as a mean 40,500 calories.

A comparison between the observed velocity constants and those calculated on the basis of the activated collision theory of bimolecular reaction is now possible. The total numbers of collisions occurring per cubic centimeter per second is given by $2n^2\sigma^2\sqrt{\pi kT/m}$, where n is the number of molecules per cubic centimeter, σ the diameter, and m the mass of the molecules. The diameter of the acetylene molecule is not given in the literature, though some scant data are available on the viscosity. Vogel (17) gives 93.5 micropoises as the value at 0°C. The temperature variation is not known, though for ethylene, which has an almost identical viscosity at 0°C., the variation with the temperature is given by the Sutherland constant of 226. Assuming the same value for acetylene, the molecular diameter at high temperatures evaluates to 3.64×10^{-8} cm. The number of effective collisions will be $e^{-E/RT}$ times the total number of collisions, and since two molecules take part in collision the rate of disappearance of acetylene will be twice this product. At 788°K. and a concentration of 1 mole per liter this product is equal to 1.33 in liters per mole per second. The value of k determined by experiment when expressed in these same units is 0.50.

TABLE 5

Ratio of observed to calculated velocity constants

REACTION	RATIO	REFERENCE
$C_2H_2 + C_2H_2$	1:3	
$C_2H_4 + H_2$	1:220	(10)
$C_2H_4 + C_2H_4$	1:370	(9)
$C_4H_6 + C_4H_6$	1:10,300	(15)
$C_5H_8 + C_5H_8$	1:530	(16)

The ratio of the observed to the calculated velocity constants, 1:3, may be compared with similar ratios found in other association reactions. Vaughan (16) has recalculated many of the available data and summarized the results on a comparable basis. In table 5 are listed the known examples.

The smallness of the ratio for acetylene is in harmony with the simplicity of the molecule, and though too much reliance may not legitimately be placed on the actual figure (the limits are probably 1 and 1:10) the position of the reaction in the series is significant.

HYDROGENATION

In the reactions with hydrogen measurements were made over the same temperature range, using different mixtures of acetylene and hydrogen.

Thus mixtures were made up which were approximately 1:1, 1:8, 1:16, and 1:24 acetylene to hydrogen, and each mixture was investigated over the whole temperature range and at partial pressures of the acetylene from about 20 to 70 mm. The observed end-point, that is, the ratio of the pressure decrease to the partial pressure of acetylene, varied with both temperature and composition, as is illustrated in table 6.

To discuss these figures as well as the subsequent treatment necessitates a consideration of the possible reactions which might occur. In the first place polymerization of acetylene will be proceeding, accompanied by the decomposition mentioned earlier. Since under the experimental conditions the partial pressures of acetylene used are rather small, a larger proportion of decomposition might be suspected as compared with that in the previous work with acetylene alone. In this connection Bone and Coward (1) and Pring and Fairlee (11) claim that decomposition is favored relative to polymerization by the presence of hydrogen. In the second place, hydrogenation of acetylene to ethylene should occur. The reaction is reversible, but the equilibrium constant at the temperatures in this study is of the order of 10^7 (5) and the reverse reaction may thus be neglected. Hydrogenation of ethylene to ethane might be expected, as well as the possible hydrogenation of the acetylene polymers. It would seem necessary to invoke all of these to account for the observed end-points. However, a study of the individual rates of pressure change showed there was a very gradual approach to the end-point, a pressure decrease approximately equal to the initial acetylene pressure occurring relatively rapidly, followed by a considerably slower decrease for many hours and even days before any semblance of an end-point was eventually reached. It is probable that the major reactions occurring in this early stage involve acetylene polymerization, decomposition, and hydrogenation almost exclusively, and since little is known of the decomposition it can only be grouped with the hydrogenation and allowance made for the known polymerization. The relative occurrence of these two tendencies may be roughly estimated.

TABLE 6

Variation in observed end-point with temperature and composition

TEMPERATURE	MIXTURE $C_2H_2 \cdot H_2$	END-POINT	TEMPERATURE	MIXTURE $C_2H_2\ H_2$	END-POINT
°*C.*			°*C.*		
495	1:1	0.81	515	1:16	1 93
495	1:8	1 24	515	1:24	2 28
495	1:16	1.60	535	1:8	1 51
495	1:24	1 98	535	1:16	2 15
515	1:8	1 32	535	1:24	2 51

Assuming, in anticipation of later results, that the hydrogenation is bimolecular, the rate of disappearance of acetylene will be given by

$$-\frac{d[C_2H_2]}{dt} = k_1[C_2H_2]^2 + k_2[C_2H_2][H_2]$$

and the observed pressure change by

$$-\frac{dP}{dt} = k_1 p^2_{C_2H_2} + 2k_2 p_{C_2H_2} p_{H_2}$$

With mixtures high in hydrogen content it is apparent that the second term on the right will contribute predominatingly to the rate. Calculations, using as low a ratio as 1:10 for acetylene to hydrogen and arbitrary values of k_1/k_2, show the relative insignificance of the polymerization. The value of k_1/k_2 actually found is about 5, and it is legitimate therefore to neglect the polymerization at higher hydrogen ratios in order to approximate the value for k_2 for a more exact evaluation at the lower ratios. The method is virtually one of successive approximations. Thus, assuming only hydrogenation to ethylene to occur early in the reaction, for acetylene to hydrogen ratios of 1:32 or 1:24, the one-tenth or one-quarter lives will be the times necessary for the pressure to decrease by one-tenth or one-quarter of the initial pressure. Calculating an approximate velocity constant from these values gives a value of 5.0 for the 1:24 mixture and 5.5 for the 1:32 mixture for the ratio of the rates of polymerization and hydrogenation for the same acetylene pressure at temperatures from 495°C. to 535°C. Using this latter value and assuming the major reactions to be

$$4C_2H_2 \rightarrow (C_2H_2)_4$$
$$C_2H_2 + H_2 \rightarrow C_2H_4$$

the times taken for one-tenth of the acetylene to be hydrogenated for the various mixtures used may be evaluated. Thus for the 1:32 mixture the one-tenth life will be the time for the pressure to decrease an amount equal to 0.110 of the initial pressure, and similarly for other acetylene to hydrogen ratios. The times so found at one temperature as typical of the other temperatures are given in table 7, together with the velocity constants calculated from them by the usual bimolecular equation.

There can be no doubt that the previous assumption of bimolecularity is completely justified. Since, however, account has only been taken of the acetylene polymerization which is occurring simultaneously with the hydrogenation, and no account was taken in the above of the acetylene decomposition, more reliable estimates of the velocity constants of the hydrogenation would be obtained from data taken as early in the reaction as possible. To this end a procedure similar to that used for the polymerization was adopted, involving an extrapolation to zero time of the observed

TABLE 7

Velocity constants

Temperature, 515°C.

INITIAL C_2H_2 PRESSURE	$t_{1/10}$	k	$t_{1/4}$	k	$t_{1/2}$	k
			$C_2H_2:H_2 = 1:24$			
mm.						
27	3.78	0.00047	14.1	0.00040	31	0.00044
28.2	4.0	0.00043	14.3	0.00038	34	0.00039
			$C_2H_2:H_2 = 1:16$			
27.2	5.5	0.00049	19.5	0.00043	53	0.00039
37.9	5.1	0.00038	17.0	0.00036	39	0.00038
39.3	4.4	0.00043	15.5	0.00038	37	0.00038
			$C_2H_2:H_2 = 1:8$			
29.7	12.0	0.00040	35.5	0.00040	93	0.00037
41.9	9.5	0.00040	28.0	0.00039	73	0.00037
60.4	6.2	0.00042	17.5	0.00044		
665.	5.8	0.00041	16.5	0.00042	45.5	0.00037

TABLE 8

TEMPERATURE	$k_{\text{hydrogenation}}$	E
°C.		
495	0.00019	43540
505	0.00028	40410
515	0.00039	43010
525	0.00055	41470
535	0.00076	

rate of pressure change and calculation from this value of the velocity constant. Thus

$$-\frac{dP}{dt} = k_1 p^2_{C_2H_2} + 2k_2 p_{C_2H_2} p_{H_2}$$

Since k_1/k_2 is approximately 5.5

$$k_2 = \frac{-dP/dt}{5.5 p^2_{C_2H_2} + 2p_{C_2H_2} p_{H_2}}$$

In this way the probability that the values of k_2 are vitiated by the occurrence of acetylene decomposition is reduced as far as would seem possible. The constants so obtained are presented in summary in table 8 for the five temperatures studied. The energies of activation for the succeeding temperature intervals are also included and give an average value of 42,000 calories. This value may be compared with that calculated by Sherman and Eyring (13) on the basis of quantum mechanics, namely 46,400 calories. This discrepancy is not unexpected in that the calculated value relates to 0°K. and depends on the choice of 10 per cent for the coulombic energy. Furthermore the value found is very close to that obtained by Pease for ethylene hydrogenation, 43,200 calories.

The comparison between the observed velocity constant at a particular temperature and that calculated on the basis of collision theory may again be made as in the previous case. Taking the total number of collisions occurring per cubic centimeter per second between unlike molecules as $2N_1N_2\sigma_{12}^2\sqrt{2\pi kT(m_1+m_2)/m_1m_2}$, where N_1 and N_2 are the numbers of molecules per cubic centimeter of acetylene and hydrogen respectively, of masses m_1 and m_2, σ_{12} is the mean of their two diameters, so with 3.6×10^{-8} cm. as the diameter of acetylene and 1×10^{-8} cm. for hydrogen, using 42,000 calories as the energy of activation, it is calculated for the temperature 788°K. that the velocity constant should be 0.724 liter mole^{-1} sec.^{-1} The observed value in these same units is 0.252, whence the ratio is again found to be approximately 1:3, also in harmony with the values for other reactions previously quoted in view of the simplicity of the molecules partaking in the reaction.

SUMMARY

The homogeneous thermal polymerization of acetylene and its hydrogenation have been investigated in the temperature range 495°C. to 535°C. The principal processes are interpreted as bimolecular with energies of activation of 40,500 and 42,000 calories, respectively. The efficiency of the association is high, in that the ratio of the observed rates to those calculated on the basis of activated collisions is 1:3 in both cases.

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THE SYSTEM PYRIDINE-ACETIC ACID. IV

BOILING POINTS

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In earlier papers by one of the present authors and his collaborators (8, 9, 10), the viscosities, melting points, and electrical conductance of mixtures of pyridine and acetic acid have been reported. The object of these investigations was to determine the number and kind of complexes existing in this system. Of the methods of investigation used so far, all indicate the existence of a complex with a composition between 80 and 85 mole per cent acetic acid. The melting point–composition diagram shows some evidence of the existence of a second complex with a composition of 50 mole per cent acetic acid. This report deals with an extension of the work to include boiling point data for the system.

The presence of a stable complex should decrease the vapor pressure of a given mixture, at constant temperature, below the vapor pressure of the mixture if it were ideal or even only approximately so. This vapor pressure lowering should be most pronounced when the largest amount of the complex is present. This condition would manifest itself by the formation of a maximum boiling point mixture. Highly unstable complexes would probably have little or no effect in the production of a maximum boiling point, since such complexes would be very largely dissociated at the high temperatures at which the mixtures boil. It is also possible, in case the system does show a maximum boiling point, that the composition of the mixture having such maximum boiling point may change with pressure, owing to the variation in the extent of dissociation with the different boiling temperatures corresponding to the different pressures.

Gardner (5) concluded, from boiling point measurements on this system, that a compound of the composition $2C_5H_5N \cdot 3CH_3COOH$ was formed. He reports that a large part of this mixture distills at an approximately constant temperature of 139–140°C., with constant composition. André (1, 2), on the basis of boiling point measurements, reports a complex of the same composition. In the present paper, we have redetermined the boiling point–composition relations for the system, and have investigated the effect of pressure changes on the composition of the mixture showing the maximum boiling point.

MATERIALS

The pyridine and acetic acid used in these measurements were purified in the manner described in an earlier paper (9).

APPARATUS

The boiling point apparatus described by Nelson (6) was modified slightly and used for the boiling point measurements. A special glass distillation apparatus was built and used to obtain the composition and boiling point of the maximum boiling mixture at different pressures.

TABLE 1

Boiling points of pyridine–acetic acid mixtures

BOILING TEMPERATURE AT 760 MM. PRESSURE	COMPOSITION OF RESIDUE MOLE PER CENT ACID	COMPOSITION OF DISTILLATE MOLE PER CENT ACID
°*C.*		
117.85	100.0	100.0
122.30	92.3	99.2
126.80	86.7	97.0
130.15	81.4	92.0
134.00	74.4	86.1
136.95	66.8	76.0
137.25	65.1	72.2
138.05	62.0	66.5
138.40	57.6	57.3
138.35	56.2	54.4
138.00	53.7	47.0
137.20	49.3	37.6
135.05	43.0	26.8
130.70	32.2	14.0
125.5	23.4	6.2
120.55	13.8	2.5
115.00	0.0	0.0

Pressures were measured to 1 mm. mercury by means of a mercury manometer.

All thermometers used were carefully checked against thermometers calibrated by the Bureau of Standards.

METHOD

All solutions were made up by weight, and compositions are expressed in mole per cent acetic acid, accurate to 0.001 per cent.

The boiler and receiver of the Nelson apparatus (6) were filled with the same mixture and distillation then carried out (at 760 mm.) until equilibrium was established between the liquid in the two containers. Constancy of boiling point at 760 mm. pressure was taken as sufficient evidence that the equilibrium condition had been reached. About three hours were required for the attainment of equilibrium. The boiling temperatures were read to 0.05°C. When the equilibrium temperature was reached, samples the of residue and distillate were removed from the apparatus and analyzed. This procedure was repeated for mixtures over the entire range of composition, except for mixtures in the immediate vicinity of the maximum boiling point mixture (see table 1).

The boiling point and composition of the maximum boiling point mixture could not be obtained with the Nelson apparatus except by accident. A large volume of mixture of the approximate maximum boiling point composition was placed in the special all-glass still and the mixture boiled, at constant pressure (760 mm.), until a constant boiling point was reached. Samples of residue and distillate were taken as before (see table 2).

TABLE 2

Maximum boiling point mixtures of pyridine and acetic acid

PRESSURE	BOILING POINT		COMPOSITION, MOLE PER CENT ACETIC ACID	
	Initial	Final	Initial	Final
mm Hg	°C.	°C.		
760	138 25	138 40	59 4	58 4
760	138 20	138 35	55 0	58 4
760	125 00	138 35	89 0	58 4
800	139 85	140 05	59 4	58 4
570	129 40	129 55	59 4	58 9
380	117 50	117 55	59 4	59 5
190	99 50	99 55	59 4	60 2
120	87 10	87 15	59 4	60 8

After the composition of the maximum boiling point mixture had been determined, the procedure was repeated at pressures of 800, 570, 380, 190, and 120 mm. of mercury.

The residue and distillate samples were analyzed by measuring their densities and comparing these values with the measured values of the densities of mixtures shown in table 3 and figure 3.

EXPERIMENTAL RESULTS

Figure 1 shows the pyridine–acetic acid system to exhibit a maximum boiling point of 138.35 ± 0.05°C. at 58.4 mole per cent acetic acid, under a pressure of 760 mm. The maximum boiling mixture contains slightly less acetic acid than the composition reported by Gardner (5) and André (1, 2). The maximum boiling temperature is also slightly less than the value reported by these workers. Figure 2 shows the manner in which the composition of the maximum boiling mixture changes with changes in pressure. At pressures less than 760 mm. the composition of the maximum boiling mixture shifts slightly in the direction of higher acetic acid content, approximating a mixture of 3 moles of acetic acid and 2 moles of pyridine

TABLE 3

Densities of pyridine–acetic acid mixtures at 32.38°C.

ACETIC ACID MOLE PER CENT	DENSITY	ACETIC ACID MOLE PER CENT	DENSITY
0.000	0.9720	77.722	1.0640
6.345	0.9769	78.698	1.0652
12.566	0.9818	79.734	1.0664
18.529	0.9870	80.771	1.0676
24.359	0.9923	81.543	1.0684
29.943	0.9976	82.221	1.0690
35.225	1.0032	82.669	1.0693
40.268	1.0089	83.720	1.0700
45.440	1.0149	84.773	1.0704
50.004	1.0209	85.234	1.0707
54.890	1.0273	85.894	1.0711
59.594	1.0345	86.470	1.0711
63.927	1.0415	86.790	1.0716
68.202	1.0487	88.568	1.0700
72.438	1.0558	90.710	1.0676
74.790	1.0595	94.834	1.0583
76.256		100.00	1.0380

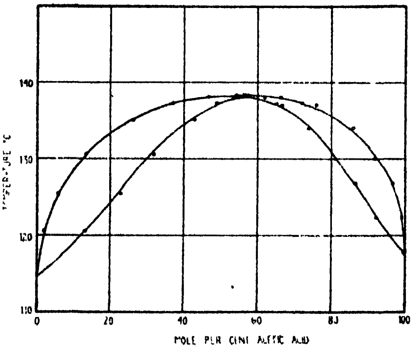

FIG. 1

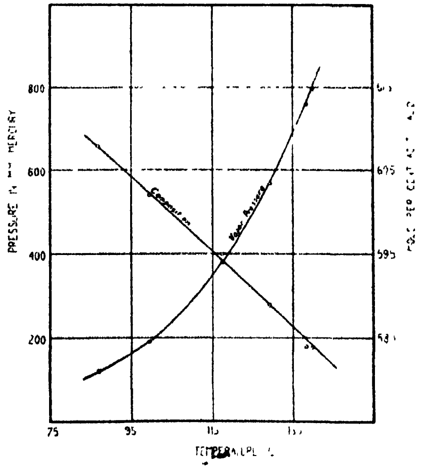

FIG. 2

FIG. 1. BOILING POINT CURVE FOR PYRIDINE AND ACETIC ACID MIXTURES

FIG. 2. MAXIMUM BOILING POINT MIXTURES OF PYRIDINE AND ACETIC ACID

at a pressure of 120 mm. This variation in composition of the maximum boiling mixture with changes in pressure precludes the existence of any very stable complex at this point.

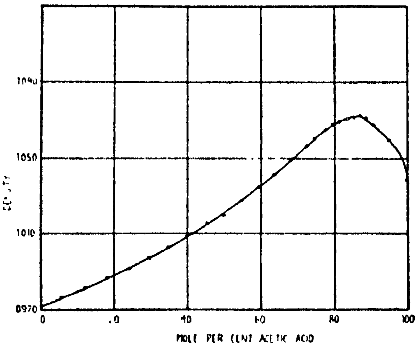

FIG. 3. DENSITIES FOR PYRIDINE AND ACETIC ACID MIXTURES AT 32.38°C.

TABLE 4

Complexes in the system pyridine–acetic acid

COMPLEX	METHOD OF IDENTIFICATION	INVESTIGATOR
1. Formula not given. Near 80 mole per cent acetic acid	Electrical conductance	Trifonov and Cherbov (12)
2. $3C_5H_5N \cdot rCH_3COOH$ (r unknown)	Electrical conductance	Sackhanov (7)
3. $2C_5H_5N \cdot 3CH_3COOH$	Boiling point Boiling point Boiling point	André (1, 2) Gardner (5) Swearingen and Ross
4. $C_5H_5N \cdot rCH_3COOH$ (r equals 4 or 5)	Viscosity	Tsakalotoes (11); Faust (4); Dunstan (3); Swearingen and Heck (8)
	Electrical conductance	Swearingen and Ross (10)
	Fusion point	Swearingen and Ross (9)
5. $C_5H_5N \cdot CH_3COOH$	Fusion point	Swearingen and Ross (9)

Table 4 facilitates a comparison of the complexes previously reported in the literature and those obtained in the current investigation.

The melting point–composition data, without doubt, furnish the most reliable basis for speculation and comment. These data point quite conclusively to the existence of the simple pyridonium acetate. While the flatness of the melting point–composition curve at the dystectic point indicates considerable dissociation of this complex, even at its melting point, there is yet the possibility that a sufficient amount of the complex persists, even at 138.35°C., to account for the maximum boiling point.

The second complex, indicated by the melting point–composition curve, has a composition between 80 and 85 mole per cent acetic acid, probably either at 80 or 83.3, since these compositions correspond to complexes $C_5H_5N\cdot 4CH_3COOH$ and $C_5H_5N\cdot 5CH_3COOH$, respectively. This complex is highly unstable, as shown by its incongruent melting point and high electrical conductivity in this region. The presence of this unstable complex is in no way revealed on the boiling point–composition diagram.

Thus, the boiling point data would seem to indicate dissociation of this complex into CH_3COOH and $C_5H_5N\cdot CH_3COOH$ molecules, while the conductance maximum would indicate dissociation into ions.

On the basis of all of the experimental evidence available, the behavior of this system might be formulated in the following equation:

$$\begin{array}{cl}
2C_5H_5N + 2rCH_3COOH & \\
\uparrow\downarrow & \\
2(C_5H_5N\cdot CH_3COOH) + (2r - 2)CH_3COOH & \text{(Indicated by freezing points)} \\
\uparrow\downarrow & \\
2C_5H_5N\cdot(2r - s)CH_3COOH + sCH_3COOH & \text{(Indicated by boiling points)} \\
\downarrow\uparrow & \\
2(C_5H_5N\cdot rCH_3COOH) & \text{(Indicated by conductance and viscosity)} \\
\downarrow\uparrow & \\
X^+ + Y^- &
\end{array}$$

where r equals 4 or 5, s equals 5 or 7 respectively, and X and Y are conducting ions.

SUMMARY

The boiling point–composition relations for pyridine and acetic acid mixtures have been determined over the entire range of composition.

A maximum boiling point mixture containing 58.4 mole per cent acetic acid was found to boil at 138.35°C., under a pressure of 760 mm.

No complexes indicated by viscosity, melting point, or conductance measurements are indicated on the boiling point–composition curve.

Data are presented to show that the composition of the maximum boiling mixture is influenced by pressure.

The densities of mixtures of pyridine and acetic acid have been determined at 32.38°C.

A résumé of all complexes reported for this system have been included.

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INFLUENCE OF CONCENTRATION AND AGE ON SOME COLLOIDAL PROPERTIES OF FERRIC CHLORIDE SOLUTIONS

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INTRODUCTION

The effect of dialysis and aging on particle size and constitution of colloidal ferric oxide sols prepared by a condensation method has been investigated by Nichols, Kraemer, and Bailey (4), who found that during aging the particle size distribution shifts slightly toward larger sizes, the formation of secondary aggregates being more pronounced in concentrated sols. The age of the stock solution of ferric chloride was observed to affect the particle size of the resulting ferric oxide. The particles gradually decreased in size with increasing age of the stock solution, and it was suggested tentatively that this was due to the formation of more and more nuclei therein.

Condensation methods for the preparation of colloidal suspensions depend upon creation of a supersaturation of the condensable phase, together with some starting points or nuclei to serve as centers for growth. The number of particles produced and the degree of dispersity depends upon the number of these starting points or centers. Further, the distribution of size of the condensed particles depends upon the rate of migration of material to the centers, taking into account the amount of dissolved material and the number of condensing centers. Nuclei are often produced by the condensation process itself, but in some cases artificial centers can be introduced. The rate at which the nuclei appear affects the distribution of the size of the particles, since those introduced or formed first are supplied with more material for building particles than are those formed later, and will consequently become larger. If it were possible to introduce all of the centers at the beginning, before the condensation process sets in, and to avoid spontaneous production of centers, one might expect to get much more uniformly sized particles. In fact, such principles have been used in Zsigmondy's nuclear method of preparing gold sols, with the result that fairly uniformly sized particles were obtained.

The object of the present investigation was to determine the effect of age and concentration of ferric chloride solutions on the pH values, the mobility, and the number of colloidal particles. The selection of ferric chloride systems for this work seemed desirable for two reasons: first, their property of spontaneous production of ultramicroscopically visible particles on standing at room temperature; and second, their frequent use in preparation of colloidal ferric oxide by high temperature hydrolysis.

TABLE 1

Measurements on ferric chloride solutions

AGE	NO. OF PARTICLES PER CC. $\times 10^{-9}$	MOBILITY μ/SEC./V./CM.	pH
	M/1000 ferric chloride		
0 hours	0.4	3.6	3.02
20 hours	0.6	3.1	2.70
2 days	0.7	3.0	2.66
7 days	38.	2.9	2.62
12 days	86.	2.7	2.49
21 days	107.	2.5	2.56
	M/100 ferric chloride		
0 hours	4.7	4.2	2.37
20 hours	168.	3.7	2.10
2 days	655.	3.6	2.08
7 days	849	3.6	2.00
14 days	1090.	3.0	1.99
21 days	1155.	2.8	1.98
49 days	1336.		1.96
	M/10 ferric chloride*		
0 hours	6.0	3.4	1.80
20 hours	56.	2.8	1.61
2 days	59.		1.65
7 days	69.		1.64
14 days†	93.		1.63
21 days	405.		1.58

* Mobility measurements for this concentration could not be accurately made because of a drift in the liquid due to electrolysis of the ferric chloride solution.

† Precipitation occurred.

EXPERIMENTAL

Ferric chloride solutions of three concentrations, *M*/1000, *M*/100, and *M*/10, were prepared, and immediately after preparation measurements of the number of particles (1), electrophoretic velocity (2), and pH (3) were made by methods previously described. Similar measurements were made at definite time intervals thereafter up to twenty-one days, the solutions being allowed to stand undisturbed at room temperature. The results of these measurements for the above concentrations are given in table 1.

Table 2 shows the results of measurements on ferric chloride solutions and the resulting high-temperature hydrolysis products. Solutions of *M*/1000 and *M*/100 ferric chloride were prepared as before and similar measurements made. Then definite quantities of these solutions (50 cc. of *M*/100 and 100 cc. of *M*/1000), were dropped slowly into 950 cc. and 900 cc. respectively of boiling water, following the usual method of preparing ferric oxide sols. Number of particles, migration velocity, and pH were then determined for these hydrolysis products.

TABLE 2

Measurements on ferric chloride solutions

AGE	NO. OF PARTICLES PER CC. $\times 10^{10}$		MOBILITY μ/SEC./V./CM.		pH	
	Original	Product	Original	Product	Original	Product
			M/1000 solution			
0 hours	0.04	0.4	3.0	1.9	3.02	3.40
20 hours	0.06	0.9	2.9	2.3	2.70	3.46
2 days	0.07	1.0	2.8	1.8	2.68	3.47
7 days	2.2	18.8	3.0	2.2	2.63	3.41
14 days	3.4	37.7	2.8	2.4	2.58	3.34
21 days	10.1	117.0	2.5		2.56	3.30
			M/100 solution			
0 hours	0.47	11.8	4.1	3.2	2.36	2.84
20 hours	3.5	85.	3.6	3.0	2.12	2.77
2 days	67.3	1151	3.1	2.9	2.09	2.71
7 days	88.1	1640.	3.1	2.8	2.00	2.60
14 days	107.3	1992	3.0	2.7	1.99	2.56
21 days	118.4	2302	2.9	2.7	1.98	2.50

DISCUSSION

As was previously mentioned the rate of growth of colloidal particles is determined by. the number of nuclei present and the degree of supersaturation of the system. In the system under consideration there are no nuclei present at the starting point, hence they must be produced by growth from the ferric chloride molecules in solution. The rate of nucleus formation is itself dependent upon the degree of supersaturation, so that ferric chloride solutions of different concentrations should exhibit initial growth stages of different lengths. When the particles have reached the minimum size necessary for nuclear action, i.e., when the initial growth stage is over, the particle growth is governed by the concentration of dissolved matter. If this concentration is sufficiently great a sudden appearance of particles will be evident.

If a solution contains C gram-equivalents of ferric chloride per liter and the degree of hydrolysis is denoted by x, the following expression may be written[1]

$$c_{\mathrm{Fe(OH)_3}} = xC$$

$$c_{\mathrm{H^+}} = 3xC \text{ (assuming complete dissociation)}$$

$$c_{\mathrm{Fe^{+++}}} = \alpha\,(1 - x)C$$

where α denotes the degree of dissociation of ferric chloride. Therefore,

$$x = \frac{c_{\mathrm{H^-}}}{3C} \text{ and } c_{\mathrm{Fe^{+++}}} = \alpha\left(1 - \frac{c_{\mathrm{H^+}}}{3C}\right)C = \alpha\left(C - \frac{c_{\mathrm{H^+}}}{3}\right)$$

The amount of ferric hydroxide formed is then directly proportional to the concentration of hydrogen ions. If the amount of ferric hydroxide in colloidal form is assumed to be directly proportional to the amount of ferric hydroxide in true solution, a linear relation should exist between the hydrogen-ion concentration and the number of particles observed under the ultramicroscope.[2] In figure 1 these quantities are plotted for $M/10$, $M/100$, and $M/1000$ solutions. Apparently the linear relationship is valid for certain stages of the process. It will be observed, however, that the initial points are in each case off the curve. Speculation regarding the reason for this behavior must be reserved until more experimental data can be obtained.

A consideration of the relationships between the age of the solution and the number of particles, graphically represented in figure 2, should lead to a more intimate understanding of the mechanism of particle formation. The abrupt changes in the courses of the curves indicate that the process may be considered as a summation of steps, rather than one step which might be represented by a continuous function. It is well known that precipitation proceeds slowly until the nuclei have reached a size sufficient to function as condensation centers. In this connection Nordenson (5), during conductivity studies on the formation of gold sols, observed a similar stepwise character in the course of particle formation. He concluded that after the original precipitation the gold molecules slowly condense to colloidal gold particles until a great number of particles have reached the minimum size of nuclear action. After the nuclear limit is reached the reduction process proceeds rapidly, depositing the rest of the gold on the gold nuclei formed during the growth period. Nordenson demonstrated that the nuclear growth period could be arrested at will by the addition of colloidal gold particles, which then functioned as condensation nuclei causing a rapid particle growth. If it be assumed that a similar series of steps holds for the growth of colloidal particles from ferric chloride solutions, then the different stages for $M/100$ solution (figure 2) may be identified thus: (1) A to B—a slow nuclear growth stage; (2) B to C—a rapid condensation stage with large increase in the number of visible particles; (3) C to D—a slow growth stage similar to (1). Upon longer standing it might be expected that a fourth stage, similar to (2), would occur. Although no such stage was observed for the relatively short periods used in this investigation, a year-old sample of $M/100$ ferric chloride, originally clear, was found to have undergone marked precipitation, while still retaining a large number of colloidal particles in the supernatant liquid.

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[1] Making the simplifying assumption that no basic chlorides are formed.

[2] The observed number of particles may not exactly represent the amount of colloidal material, since obviously a number of amicrons may be present. The reaction is of course very complicated, notably because basic chlorides of varying composition are formed. The basicity of the latter possibly changes with aging of the solution, and this is accompanied by changes in the hydrogen-ion concentration. The rate of the reaction is opposed by increased hydrogen-ion concentration, and is favored by adsorption (which removes hydrogen ions from solution) and factors which tend to increase the adsorbing surface, such as particle formation. It is apparent from the data, however, that a consideration of the simple hydrolytic equilibrium given above cuts across these secondary phenomena and establishes a relation between the rate of particle formation and the hydrogen-ion concentration.

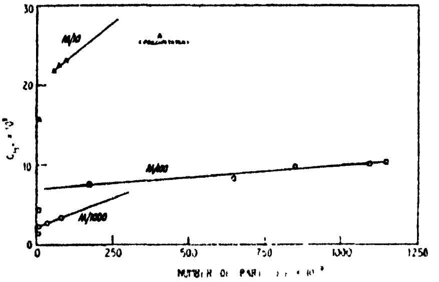

FIG. 1

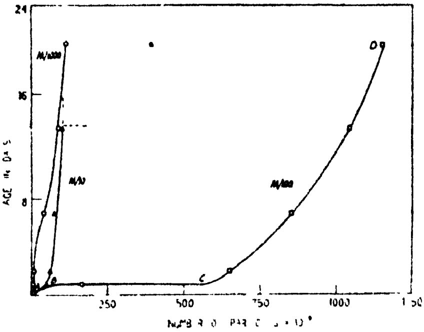

FIG. 2

It is a well-known fact that normal growth processes follow an exponential law. This behavior affords a means of differentiating more rigidly between successive stages in the curves of figure 2. If y denotes the number of particles and t denotes the time (age), the law of exponential growth is given by

$$y = y_0e^{ct}$$

where y_0 represents the number of particles at the beginning of the growth stage and c is a constant.

Taking logarithms,

$$\ln \frac{y}{y_0} = ct$$

$$2.303\log y = ct + 2.303\log y_0$$

so that plotting log y against t should yield a straight line. This operation is carried out in figure 3. It will be observed that the linearity is quite good

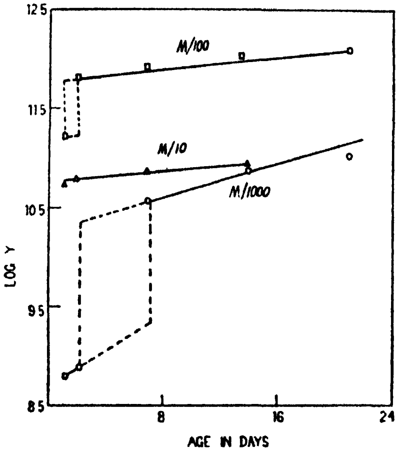

FIG. 3

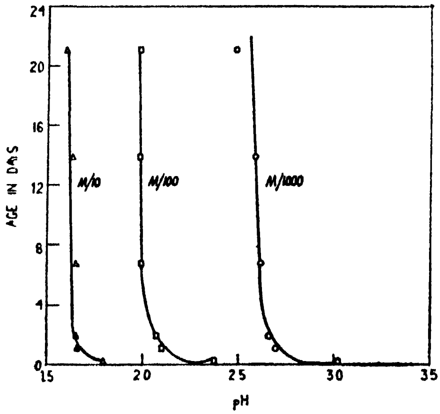

FIG. 4

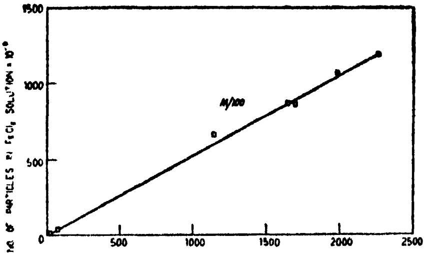

FIG. 5

in all cases. The stepwise character of the process is clearly shown by the abrupt discontinuities in the curves. The fact that the number of particles in the $M/1000$ solution is smaller than the number in either of the other two solutions at any stage appears reasonable, as does the fact that the stepwise character of the curve (figure 2) is less pronounced. However, the position of the curve for the $M/10$ solution is anomalous.

The graphical representation of the relation between age and pH of the solutions is shown in figure 4. The relative positions of these curves for the different concentrations of solutions are quite normal, and the similarity of the curves is good. They are all typically logarithmic curves, the initial drop corresponding to a more rapid hydrolysis at the beginning of the process.

An examination of the tables reveals that with increasing age of the ferric chloride solutions a gradual decrease occurs in the migration velocity of the particles. At the start, when few particles are present, adsorption of positive ions (Fe^{+++} and H^+) is great, resulting in a high particle velocity. As more particles form, ferric ions are constantly used up, making less available for adsorption. At the same time the concentration of the solution gradually becomes less. With more particles and less available ions the charge on each particle is lowered, with a proportional drop in the migration velocity.

The results in table 2 show that the number of particles in the hydrolysis product of a ferric chloride solution is governed by the number of particles present in the original stock solution. This is shown graphically by the linear curve in figure 5.

SUMMARY

1. An investigation of the effect of age and concentration on some of the colloidal properties of ferric chloride solutions has been made. Ultramicroscopic methods were used to follow changes in particle number and particle velocity, while changes in pH were measured with a glass electrode.

2. Spontaneous formation of nuclei was found to take place in all concentrations of ferric chloride studied. The number of these nuclei present at the start was affected by the original concentration of the solution.

3. As the solutions of ferric chloride aged the number of colloidal particles increased in a stepwise manner.

4. The hydrogen-ion concentration of the solutions increased as hydrolysis proceeded. This increase when plotted against the increase in particle number gave an approximately linear relation.

5. Aging of the ferric chloride solutions resulted in a lowering of the electrophoretic velocity.

6. The number of particles in the ferric chloride solutions influenced the number of particles in the resulting high-temperature hydrolysis product.

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THE INTERMEDIATE STAGES OF ALDEHYDE OXIDATION. I

THE CATALYTIC ACTION OF MANGANESE CATALYST IN THE VARIOUS STAGES OF THE PROCESS OF ACETALDEHYDE OXIDATION

M. J. KAGAN AND G. D. LUBARSKY

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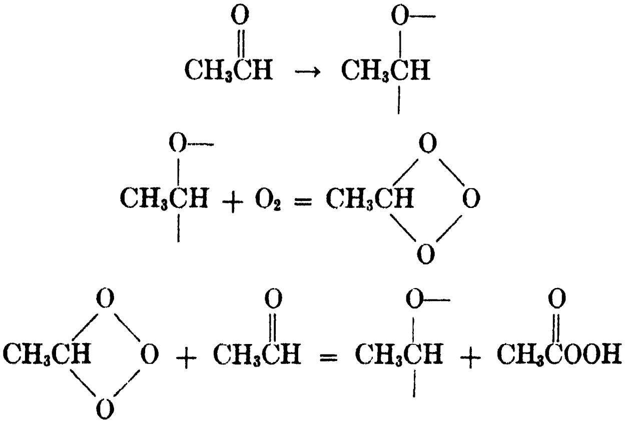
In the autoxidation of acetaldehyde we are concerned with the reaction of the formation of peracetic acid.

According to Bodenstein (2), the following chain mechanism takes place



(1)

(2)

(3)

Molecular oxygen adds to the active form of aldehyde (1), producing the active form of peracetic acid (2), in agreement with the theory of Bach (1) and Engler (4). The latter reacts with a normal molecule of acetaldehyde forming again an active aldehyde molecule and the final product (3). The peracetic acid obtained can in turn oxidize aldehyde further, forming acetic acid. The process of oxidizing acetaldehyde by oxygen directly to acetic acid in the presence of a catalyst is widely used in industry. For the investigation of the mechanism of this process, the study of the kinetics of not only the first stage of the formation of peracetic acid is important, but also the second stage, the interaction of peracetic acid with acetaldehyde.

We have made a special study of the second stage of this process (see the following article), and have found that the interaction between peracid and aldehyde proceeds also in two stages (a) and (b): (a) The addition of a molecule of aldehyde to the peracetic acid and the formation of an intermediate product of a peroxide character. The activation energy of this bimolecular reaction is 7000 calories, and its rate is higher than that of the second stage. (b) The decomposition of the intermediate product with the formation of two molecules of acetic acid. The activation energy of this monomolecular reaction is 15,000 to 16,000 calories.

The oxidation of acetaldehyde by oxygen to acetic acid at both low and room temperatures takes place at a slow rate, and in the absence of catalysts leads to the accumulation of peroxides. Hence it follows that the transformation of the peroxides to acetic acid proceeds more slowly than their formation. Bodenstein determined the activation energy of the first stage of acetaldehyde oxidation—the chain reaction of peracetic acid formation in the gaseous phase at about 10,000 calories.

In view of these facts we came to the conclusion that the study of the action of manganese catalyst, which is successfully applied for the oxidation of acetaldehyde to acetic acid, must follow the line of investigating the kinetics of the entire process of oxidation of acetaldehyde to acetic acid in the presence of a catalyst and of the influence of the catalyst on the kinetics of the separate stages of the process.

I. THE OXIDATION OF ACETALDEHYDE TO ACETIC ACID USING A MANGANESE CATALYST. ELIMINATION OF THE INDUCTION PERIOD OF THE REACTION

The experiments were carried out in the following manner: A known solution of acetaldehyde in acetic acid was sucked into a small vessel, provided with a stopcock and a small blank tube, where a small amount of the catalyst (a manganese salt) was placed. The vessel was previously evacuated and tared, and then connected by a piece of thin rubber tubing with a bomb of oxygen (2 liters), equipped with a manometer. Both the bomb and the reaction vessel were placed in a water thermostat. The vessel was then fastened to a vertical shaking machine (length of stroke, 5 cm.), and shaken in the thermostat at a rate of about 500 strokes per minute. The particles of the catalyst were washed down at the first stroke, and this moment was fixed as the beginning of the experiment. As the reaction proceeded, fresh portions of oxygen were automatically sucked from the bomb into the vessel, owing to the decrease in pressure above the liquid in the vessel. In the experiments which were carried out at constant pressure, the readings were taken on a buret with an automatic clamp connected with a levelling vessel (figure 1).

At the beginning of the experiment the stopcock in the right bend of the manometer (C) is closed. In proportion to the absorption of oxygen, the pressure of the system falls, making contact (K), and the electromagnet E weakens the clamp. Then a small amount of water runs from the buret (F) into the beaker (D), and the pressure in the system increases to the given level, after which the mercury in the left bend falls and the electromagnet breaks contact.

In spite of the large number of experiments which were carried out, it was not possible to determine exactly the reaction velocity constants, owing to the turbulent character of the reaction which took place highly exothermically in a short time so that the vessel had no time to cool down to the temperature of the thermostat. This accounts for the qualitative character of the results obtained, which nevertheless are of fundamental interest.

The commencement of the decrease of the oxygen pressure always coincided with the appearance of a dark brown coloration of the solution.[1] In some experiments the coloration did not appear at all, and the reaction did not take place; in others it appeared some time after the beginning of the shaking (3–75 minutes), and only after its appearance did the reaction and a sharp decrease of pressure in the system take place. Thus the added salts of bivalent manganese (acetate, nitrate[2]) do not appear to be catalysts. On the contrary the catalyst is formed in the aldehyde solution which is being oxidized, and only after its formation does the high reaction rate take place. The composition of the brown solution acting as catalyst

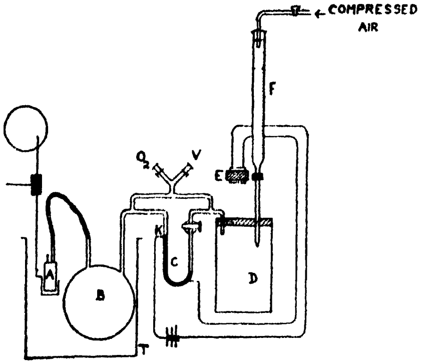


Fig. 1

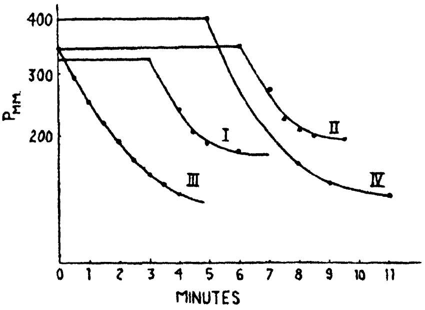


Fig 2

Fig. 1. The Apparatus

V, to vacuum pump

Fig. 2. The Oxidation of Acetaldehyde in Acetic Acid Solution

I, catalyst $Mn(NO_3)_2$ at 25°C., induction period 43 minutes; II, catalyst $Mn(NO_3)_2$ at 25°C., induction period 73 minutes; III, catalyst $(CH_3COO)_3Mn$ at 15°C.; IV, catalyst $(CH_3COO)_3Mn$ at 15°C. in acetic acid and 10 per cent water solution, induction period 62 minutes.

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[1] The formation of the brown solution had been observed by Baeyer and Williger when introducing manganese acetate into a solution of perbenzoic acid.

[2] In a paper by M. J. Kagan and N. M. Morozov (6) it was shown that the activity of manganese nitrate as a catalyst of this process is 50 per cent greater than that of manganese acetate.

in this reaction was found to be an acetic acid salt of trivalent manganese. In the presence of this compound no induction period, which occurred in other experiments, was observed, as is shown by curves in figure 2. The accumulation of this compound evidently takes place during the induction period.

It is obvious that anything causing the decomposition of manganic acetate, $(CH_3COO)_3Mn$, must tend to lengthen the induction period. Thus, it was shown that the presence of water causes an induction period. Water decomposes maganic acetate, giving a precipitate of manganese hydroperoxide. When about 10 per cent of water was added to the solvent (acetic acid), a prolonged induction period was produced, even in the case when manganic acetate was used as catalyst (see figure 2, curve IV).

The oxidation of bivalent manganese to the trivalent form occurs under the action of peracetic acid, which is formed during the oxidation of acetaldehyde by oxygen. An acetic acid solution of manganic acetate may be readily prepared by the action of peracetic acid on manganous acetate, the peracetic acid being decomposed very turbulently. This fact cannot but influence the mechanism of the oxidation process (see below). The preparation of manganic acetate and its isolation in a pure state have been stated in detail by Christensen (3).

II. INFLUENCE OF THE CATALYST ON SEPARATE STAGES OF THE PROCESS

A. The influence of the catalyst on the rate of the interaction between peracetic acid and acetaldehyde

The determinations of the velocity of the summary reaction

$$CH_3COOOH + CH_3CHO \rightarrow 2\ CH_3COOH$$

with manganese catalyst are only of a qualitative character, owing to the poor reproducibility of the numerical values of the velocity constants in different experiments. However a sharp increase of the velocity with the addition of very small amounts of the catalyst has been positively determined (see figure 3). As shown above in the case of interaction between aldehyde and peracetic acid, the formation of the addition product is the faster, while the slower stage, limiting the reaction rates, is the decomposition of the intermediate product into two molecules of acetic acid. By studying the kinetics of the decomposition of this product in the presence of the manganese catalyst, we were able to obtain more reproducible quantitative results (shown in table 1). The experiments were carried out in the following manner: The mixture of peracetic acid and aldehyde dissolved in toluene was left standing for several hours at a temperature of −30°C., as a result of which an addition product of a peroxide character was formed. For the quantitative determination of this product in the presence of peracetic acid see paper II. The kinetics of the decomposition of this product at room temperature without a catalyst was studied. Then, at a definite moment, a solution of manganic acetate in chloroform

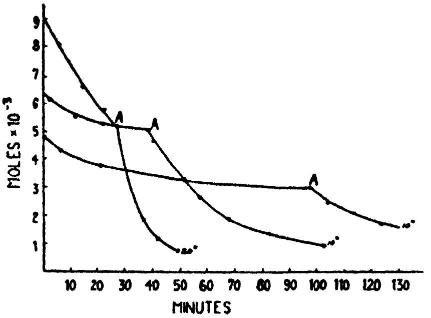


Fig. 3

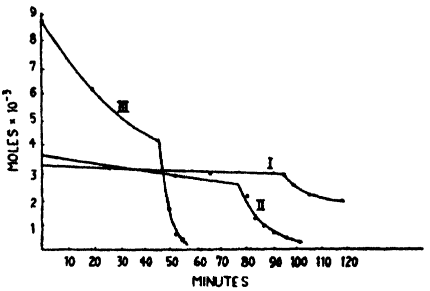


Fig. 4

Fig. 3. The Catalysis of Interaction between Peracetic Acid and Acetaldehyde

Points A correspond to the moments of pouring of the catalyst, 6 × 10^{-5} g.

Fig. 4. Catalytic Decomposition of the Addition Product (Peracetic Acid and Benzaldehyde) in Toluene Solution

I, experiment No. 119 at 10°C.; II, experiment No. 120 at 20°C.; III, experiment No. 121 at 30°C. (high concentration).

TABLE 1

Decomposition of the intermediate product (peroxide) obtained at −30°C. in a toluene solution

$t = +20$°C.			$t = +10$°C.		
Time from the beginning in minutes	Moles per liter	K (sec.$^{-1}$)	Time from the beginning in minutes	Moles per liter	K (sec.$^{-1}$)
(a) Without catalyst			(a) Without catalyst		
0	0.4015		0	0.2840	
13	0.3791	7.37 × 10^{-5}	21	0.2711	2.644 × 10^{-5}
73	0.2895	7.49 × 10^{-5}	51	0.2597	2.380 × 10^{-5}
123	0.2334	7.18 × 10^{-5}	86	0.2457	2.641 × 10^{-5}
			116	0.2351	2.436 × 10^{-5}
(b) With catalyst (manganic acetate = 0.0008 g.)			(b) With catalyst (manganic acetate = 0.0009 g.)		
0	0.2005		0	0.2130	
4	0.1504	1.2 × 10^{-3}	4	0.2004	2.545 × 10^{-4}
8	0.1169	1.05 × 10^{-3}	10	0.1830	2.825 × 10^{-4}
17	0.06466	1.1 × 10^{-3}	22	0.1548	2.325 × 10^{-4}

was introduced. The reaction rate was estimated by the disappearance of the peroxide, the content of the latter being determined iodometrically.

These data show a considerable increase in the reaction rate of this stage under the influence of the catalyst, and we are able to state quite definitely the catalytic effect of manganic acetate on the rate of this very slow reaction. Thus we have reason to suppose that the part played by the catalyst consists in accelerating the rate of decomposition of the intermediate peroxide product with the resulting speeding up of the whole oxidation process. On the other hand, a still greater catalytic effect is observed during the decomposition of the peracid, which points to the possibility of another mechanism of the catalysis.

The decomposition of peracetic acid under the action of manganous acetate

The study of the decomposition of peracetic acid in the presence of a manganese salt is of some interest in explaining the partial formation of carbon dioxide in the industrial oxidation of acetaldehyde. Moreover, as was pointed out, it may considerably influence our conception of the mechanism of the oxidizing action of peracetic acid. The decomposition was carried out at room temperature in acetic acid and water solutions in a small vessel of about 10-cc. capacity with a stopcock, connected by a piece of rubber tubing with a Hempel buret. A definite amount of the peracid solution was poured into the vessel, while manganese acetate particles were placed in the closed side-arm tube.

TABLE 2

Decomposition of peracetic acid

NO. OF EXPERIMENT	GAS CONTENT	
	CO_2	CO
	per cent	*per cent*
3	87.4	11.8
4	88 9	11 1
5	88.3	11.1
7	93.0	7 0

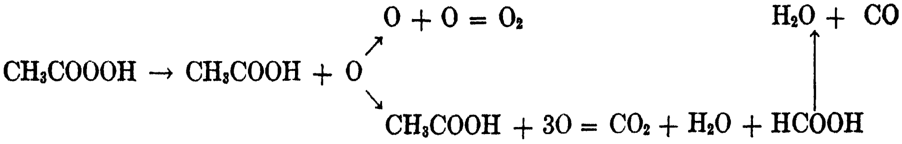
On shaking the vessel the particles of catalyst dropped into the solution, whereupon the evolution of gas began and the liquid became strongly heated. The gas was collected in the Hempel buret and afterwards analyzed for carbon dioxide, oxygen, and carbon monoxide. The results of the peracid decomposition in an acetic acid solution are very interesting. The gas evolved during the decomposition contained no oxygen, being composed chiefly of carbon dioxide and carbon monoxide, with a small percentage of hydrocarbons. The data given in table 2 are characteristic of such a process of decomposition. Immediately after coming into contact with manganous acetate, the solution acquired a dark brown color, due to the formation of manganic acetate. On diluting this solution with water, a brown-colored residue of manganese hydroperoxide is instantly formed.

A quite different process of peracetic acid decomposition was observed in a water solution; the process took place smoothly, slowly, and without any perceptible heating. When small quantities of manganous acetate were added, no manganese dioxide residue was formed, but the solution acquired the characteristic permanganate color. In case of an excess of manganous acetate the solution acquired an orange-red color, and after standing several hours or days (according to the quantity of manganous acetate) a precipitate formed. It must be noted that the decomposition of the peracid in the presence of potassium permanganate solution also proceeds very slowly. The titration of the peracid solution decomposed in the presence of potassium permanganate was as follows: 0.2 cc. of peracid solution = 4.5 cc. of thiosulfate solution (0.02 *N*); on the following day = 3.1 cc.; on the third day = 2.6 cc. The gas evolved during the reaction under these conditions was composed chiefly of oxygen, i.e., it had quite a different composition from the gas evolved during the decomposition in the acetic acid solution (see table 3). Therefore, we may conclude that oxygen forms the initial decomposition product of the peracid decomposition, which during its slow evolution is able to combine into molecules of oxygen, whereas during a turbulent evolution it oxidizes the molecules of organic compounds to carbon dioxide and carbon monoxide:

TABLE 3

Decomposition of peracetic acid

GAS CONTENT		
CO_2	CO	O_2
per cent	*per cent*	*per cent*
27.1	15.6	57.2
30.8	10.7	58.4
25.1	11.3	63.5



$$\begin{tikzcd} & O + O = O_2 & & H_2O + CO \\ CH_3COOOH \rightarrow CH_3COOH + O \arrow[ru] \arrow[rd] & & & \\ & CH_3COOH + 3O = CO_2 + H_2O + {} & & HCOOH \arrow[uu] \end{tikzcd}$$

These data are in agreement with Hatcher and Tool (5), who observed that peracetic acid is decomposed when heated, forming carbon dioxide, formic acid, and glycolic acid.

The determination of the kinetics of the decomposition of peracetic acid in an aqueous solution in the presence of manganous acetate showed that this process proceeds as a reaction of the first order and at a very slow rate, the decomposition beginning at the moment of the appearance of a pink hue of the solution (apparently due to the formation of permanganic acid). Comparison of the kinetic data obtained may be seen from table 4.

The activation energy of this process is expressed by a value approximating 12 kg-cal.

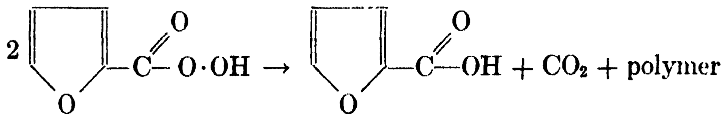
TABLE 4

Decomposition of peracid in aqueous solution in presence of manganous acetate (0.0048 g.)

Experiment 88

TIME FROM THE BEGINNING IN MINUTES	MOLES PER LITER	K (sec.$^{-1}$) × 10^6
	$t = +40°C.$	
0	0.3668	
19	0.3241	10.9
85	0.2273	8.96
98	0.2116	9.17
138	0.1673	9.8
	$t = +20°C.$	
0	0.1217	
35	0.1177	1.61
77	0.1111	2.28
113	0.1058	2.26

Observations analogous to ours were made by Milas (7) on investigating the decomposition of furo-peracid:



Solid furo-peracid was decomposed in a vacuum with the formation of a gas consisting only of carbon dioxide. In the residue was furo-acid and tarry polymer. In a weak solution of chloroform a monomolecular decomposition took place with the formation of oxygen and furo-acid. The energy of activation = 15,800 calories.

In comparing the above experimental data in the first as well as in the second version, the great influence exerted by the catalyst is observed.

In the first version, in the absence of the catalyst, we observe a high rate for the reaction of the addition of aldehyde to peracid, and a low rate of the decomposition of the addition product into 2 molecules of acetic acid. With manganese catalyst this slow process is accelerated about twenty times. It seems logical to infer that the action of the catalyst consists in the acceleration of the slowest stage, and that the scheme of the oxidation process remains the same whether it takes place in the presence or the absence of the catalyst.

$$A + O_2 = P;\ A + P = AP;\ AP = 2S^{3}$$

However, according to the above kinetics data, the decomposition of peracetic acid, using a manganese catalyst, proceeds with evolution of oxygen; only in the absence of aldehyde, which is the acceptor of oxygen, does the combustion of acetic acid take place. The decomposition of peracetic acid dissolved in glacial acetic acid occurs at an exceptionally high rate, and when aldehyde is present it may be oxidized very rapidly to acetic acid. It follows that the catalytic process may also proceed according to another scheme viz.:

$$A + O_2 = P;\ P = S + O;\ A + O = S$$

We showed above the scheme of Bodenstein for the chain mechanism of aldehyde autoxidation. The property of peracetic acid of decomposition under the action of manganese catalyst cannot but influence the chain process. At the same time the generation of the oxygen atoms may lead to a mechanism of a type differing from that proposed by Bodenstein.

The elimination of the induction period in presence of manganic acetate catalyst is of great interest. The induction period consists in the slowing down of the oxygen absorption, i.e., the delaying of the peracetic acid formation (which oxidizes Mn^{++} to Mn^{+++}). By introducing manganic acetate, the conditions are created for the reaction of the further transformation (decomposition) of peracetic acid, at the same time eliminating the induction period. It is hoped to resume this problem later in case of other oxidation reactions.

SUMMARY

1. The oxidation of acetaldehyde by oxygen in an acetic acid solution in the presence of manganese salts proceeds vigorously after the formation of a dark brown catalytic product.

2. In this process the catalytic product is trivalent manganese acetate obtained by action of peracetic acid on Mn^{++}.

3. One of the causes of the induction period of the reaction is the presence of water which decomposes the catalyst manganic acetate, forming

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[3] A = aldehyde; P = peracetic acid; S = acetic acid.

manganese hydroperoxide. In the absence of water the induction period is eliminated by the addition of a trivalent manganese salt as catalyst.

4. The rôles of the manganese catalyst may be two: on one hand it hastens the decomposition of the intermediate peroxide (product of addition of peracetic acid to aldehyde) leading to the formation of acetic acid; on the other hand it decomposes peracetic acid with the separation of active oxygen, which directly oxidizes aldehyde.

5. The formation of carbon dioxide during the oxidation of acetaldehyde by oxygen is due to the partial decomposition of peracetic acid under action of trivalent manganese. The gaseous products of peracetic acid decomposition consist chiefly of carbon dioxide ($\sim$ 90 per cent). The decomposition in the acetic acid solution takes place very turbulently and exothermically.

6. The decomposition of the peracid in the aqueous solution after the addition of manganese acetate takes place at a very slow rate. The gaseous decomposition products are chiefly oxygen ($\sim$ 60 per cent). The decomposition process is a first-order reaction and requires an activation energy approximating 12,000 calories.

7. Owing to the catalytic decomposition of peracid in the presence of aldehyde in the acetic acid solution no combustion product except acetic acid is formed, i.e., the oxygen atom oxidizes the aldehyde molecule. There seem to be good reasons for believing that such a scheme of the catalytic oxidation of aldehyde is very probable.

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THE INTERMEDIATE STAGES OF ALDEHYDE OXIDATION. II

KINETICS OF THE INTERACTION BETWEEN PERACETIC ACID AND THE ALDEHYDES

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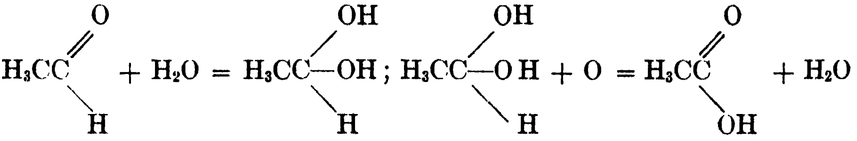
The study of the intermediate stages of aldehyde oxidation was limited chiefly to investigations of the first stage of oxidation, i.e., the formation of peracid from the aldehyde molecule and the oxygen molecule. The kinetics of the second stage of the process, the interaction between the peracid and aldehyde,

$$RCOOOH + RCHO \rightarrow 2RCOOH$$

remained unstudied.

In one of his recent papers Wieland (5) studied the process of interaction between the peracids and aldehyde. He came to the conclusion that in case of a reaction between peracetic acid and aldehyde, the reaction may be carried out with a marked velocity only in the presence of water, when aldehyde hydrate is formed. The latter is subsequently dehydrogenated by the oxygen of the peracetic acid.



$$H_3C\overset{O}{\underset{H}{C}} + H_2O = H_3C\overset{OH}{\underset{H}{C}}\text{—}OH;\ H_3C\overset{OH}{\underset{H}{C}}\text{—}OH + O = H_3C\overset{O}{\underset{OH}{C}} + H_2O$$

In the present paper, the kinetics of interaction between peracetic acid and aldehyde is studied. It was found that the formation of two molecules of acid from a molecule of aldehyde and a molecule of peracetic acid involves an intermediate reaction, viz., the formation of an addition product of the reacting molecules having a peroxide character, and that water catalytically accelerates the decomposition of this product. At the same time the kinetics of each intermediate stage was studied.

I. EXPERIMENTAL PROCEDURE

Acetaldehyde was obtained by the oxidation of alcohol by air on the surface of a copper catalyst. The pure aldehyde, redistilled several times and boiling at 20.5°C., was sealed in tared thin-walled glass ampullae.

The ampullae were weighed with the capillary glass tips sealed off; thus the weight of the aldehyde was determined to the fourth decimal. The sealed ampulla was used for the reaction during the same day; in this manner freshly distilled aldehyde was always used. The peracetic acid was obtained by action of concentrated hydrogen peroxide on acetic anhydride (3) in presence of a few drops of sulfuric acid. At the beginning the reaction proceeds very rapidly, therefore it is necessary to cool the acetic anhydride to 0°C. and then gradually to add the hydrogen peroxide drop by drop especially at the beginning. The hydrogen peroxide (Kahlbaum, 27 per cent H_2O_2) was first concentrated by distillation. The residue in the distilling flask was generally found to be 80 per cent hydrogen peroxide, which was used in preparing peracetic acid. Peracetic acid was carefully distilled in vacuum (10–15 mm.) at 24–25°C., the middle fraction being collected; in this manner a 50 per cent solution of peracetic acid in acetic acid was generally obtained, which contained almost no diacetyl peroxide. When kept in the dark at room temperature such a solution decomposes very slowly, so that even after several months the concentration changes very little.

The glacial acetic acid (f. p., 16.4°C.) used as solvent was obtained by repeated crystallization of a distilled commercial glacial acetic acid. The other solvents—benzene, chloroform, nitrobenzene, toluene—were obtained chemically pure from Kahlbaum.

The investigation of the interaction between peracetic acid and aldehyde was carried out in a small closed cylindrical vessel about 120 mm. in height and 20 mm. in diameter. The vessel was placed into a thermostat, the temperature of which was regulated with an accuracy of 0.02°C. The small cross section of the reaction vessel facilitated the maintenance of a uniform temperature of the liquid. The vessel was filled with a definite amount of peracetic acid solution.

In the reaction vessel was placed a sealed ampulla with acetaldehyde, which was broken at a given moment taken as the beginning of the reaction. At the same time another vessel with a solution of peracid of the same concentration was placed in the thermostat and stability of the acid was periodically tested. The portions from the reaction and the test vessels were pipetted with a micropipet (generally 0.1 cc.) into a previously weighed beaker containing a 10 per cent solution of potassium iodide, and after weighing (which never exceeded three minutes) the iodine evolved was titrated with 0.02 *N* sodium thiosulfate solution (2). The small additional amount of iodine evolved in standing under action of an admixture of diacetyl peroxide was generally the same for all portions, and was disregarded.

When experimenting in neutral solutions (benzene, toluene, etc.) 2 cc. of 1 *N* sulfuric acid was added to the potassium iodide solution. The concentration of acetaldehyde in the solution generally did not exceed 2–3 per cent, which corresponds to a vapor pressure of 20–60 mm. in the temperature range used (10–30°C.). These results remained unchanged if the reaction was carried out in an atmosphere of nitrogen. The investigation was carried out under ordinary conditions in a closed vessel.

TABLE 1

Kinetics of interaction between acetaldehyde and the peracid in an acetic acid solution

Experiment No. 65. Peracid, 3.377 per cent. Aldehyde/peracid = 2.12

NO. OF PORTION	TIME INTERVAL IN MINUTES	MOLES PER LITER		K (mole^{-1} cm^{3} sec.$^{-1}$)
		Peracid	Aldehyde	
		t = 288°C.		
0		0.4266	0.9043	
1	1.5	0.3711	0.8488	1.77
2	30	0.2649	0.7426	0.236
3	57	0.1948	0.6725	0.127
4	54	0.1507	0.6284	0.122
5	31	0.1320	0.6097	0.115
		t = 293°C.		
0		0.1235	0.6006	
1	21	0.1071	0.5848	0.192
2	20	0.09443	0.5722	0.181
3	20	0.08247	0.5612	0.202
4	15	0.07462	0.5533	0.200

II. KINETICS OF THE INTERACTION OF PERACTIC ACID WITH ACETALDEHYDE IN NON-AQUEOUS SOLVENTS

A. Reaction in acetic acid solutions

The interaction between peracetic acid and acetaldehyde was studied at a temperature of 10–30°C., the concentration of the solution of peracid and the ratio $\frac{\text{aldehyde}}{\text{peracid}}$ being varied from 0.5 to 3.3.

The results obtained can be described with a sufficient degree of accuracy by a second-order kinetic equation if we disregard the values obtained by calculation of the first portions taken two to ten minutes after the beginning of the reaction; as a rule these values are very high as compared with the following ones. We shall return to this point below.

Some typical experiments in acetic acid solution are given in table 1.

In table 2 the constants of the reaction rate in dependence on the temperature are given (the initial constants being disregarded).

The temperature effect is expressed by the Arrhenius equation (figure 1). The activation energy of the process is 15,400 ∓ 300 calories.

B. Reaction in other non-aqueous solutions

In order to determine the specific influence of the solvent on the reaction rate, a series of experiments was carried out using benzene, chloroform, and nitrobenzene solutions. Preliminary test experiments showed that in these solvents the peracetic acid is quite stable, and is not sensibly decomposed after standing a considerable time. Table 3 shows some of the results obtained. (Initial constants are disregarded.)

TABLE 2

Kinetics of interaction between acetaldehyde and peracid in an acetic acid solution

t	PER CENT OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	TIME OF EXPERIMENT	K (MEAN)
°C.			*minutes*	
10	2.96	1 8	120	0.0754
10	3.45	1 51	105	0.0756
15	4.91	1.35	180	0.123
15	3 38	2.12	174	0 122
20	3.12	2 2	200	0 196
20	3 38	2.1	76	0 195
25	4.8	1.45	230	0 290
25	4.77	1.61	300	0.288
30	2.5	2.43	312	0.475
30	4 32	1.39	215	0 483

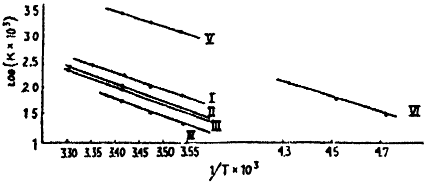


FIG. 1

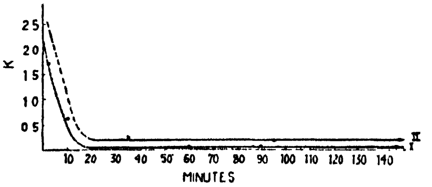


FIG. 2

FIG. 1. VALUES OF LN K PLOTTED AGAINST $1/T$

I, solvent, acetic acid; II, solvent, nitrobenzene; III, solvent, chloroform; IV, solvent, benzene; V, solvent, water (92 per cent); VI, solvent, toluene.

FIG. 2. THE REACTION VELOCITY CONSTANTS AS A FUNCTION OF TIME

I, solvent, benzene at 20°C.; II, solvent, chloroform at 30°C.

It will be noted from this table that the rate of the reaction in all the solvents is approximately equal, being lower than in the acetic acid solution. Curves obtained by plotting ln K against $1/T$ are straight lines (figure 1). The activation energy calculated from these data is approximately equal for this reaction in all solvents. Table 4 shows constants A and E of the Arrhenius equation, $K = Ae^{-E/RT}$, for various solvents.

It will be noted that in all non-aqueous solutions the velocity constants calculated from the data of the first portions (one to five minutes after commencement of the reaction) are always considerably higher than the following normal constants. When plotting the values of the velocity constants calculated according to the second-order equation, curves are obtained with a pronounced sharp inflection, after which the process goes on uniformly corresponding to the equation.

TABLE 3

Kinetics of interaction between acetaldehyde and peracid in various non-aqueous solvents

t IN °C.	PERCENTAGE OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	K (mole^{-1} sec^{-1} cm^{3})
	In benzene		
10	2.67	2.59	0.0220
15	2.88	2.48	0.0349
20	2.71	2.5	0.0610
	In chloroform		
20	1.73	2.09	0.0993
30	1.73	2.09	0.250
	In nitrobenzene		
20	1.76	3.09	0.1054
30	1.76	3.09	0.266
	In toluene		
20	2.58	3.1	0.0974

TABLE 4

The values of the constants of the Arrhenius equation for the reaction in various non-aqueous solvents

SOLVENT	A	E IN CALORIES PER GRAM-MOLE
Acetic acid	7×10^{10}	15,500
Benzene	8.5×10^{10}	16,260
Chloroform	6.6×10^{10}	16,200
Nitrobenzene	1.52×10^{11}	16,280
Water	4.56×10^{12}	16,230

This phenomenon suggested that the sharp inflection of the reaction velocity curve may be attributed to the presence of an intermediate stage, the first stage being carried out at a high rate but within the limits of the equilibrium, which is gradually shifted as the second slower stage of this reaction. This may be expressed schematically as follows:

$$\underset{\text{(rapid stage)}}{A + B \rightleftarrows AB} \rightarrow \underset{\text{(slow stage)}}{2C}$$

On this ground we might infer that if the temperature of the reaction is considerably lowered, the second stage will be slowed down in such a degree as to be almost imperceptible, while the rate of the first stage of the reaction will remain slow but quite perceptible. The reaction being obviously exothermic, the equilibrium concentration of the intermediate product will increase with cooling. Experiments absolutely confirmed this conclusion.

TABLE 5

Kinetics of interaction between aldehyde and peracid in a toluene solution

t IN °C.	PERCENTAGE OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	K (MOLE^{-1} CM^3 SEC.$^{-1}$) (MEAN)
−41	3.14	3.0	0.132
−51	3.95	2.79	0.066
−61	3.44	3.16	0.031

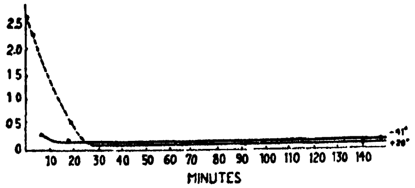


FIG. 3

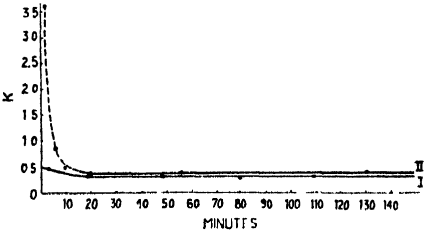


FIG. 4

FIG. 3. INTERACTION BETWEEN PERACID AND ALDEHYDE IN TOLUENE

FIG. 4. KINETICS OF INTERACTION BETWEEN VALERALDEHYDE AND PERACETIC ACID

C. *Kinetics of the reaction at low temperatures*

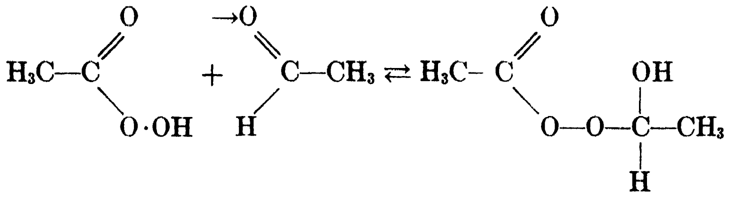
The series of experiments at low temperatures was carried out in a toluene solution, the reaction vessel being immersed in a mixture of acetone and solid carbon dioxide in a Dewar flask. The temperature was held at ±0.5°C. by means of the periodical addition of small bits of solid carbon dioxide. The test portions were taken out with a micropipet and added to a solution of potassium iodide acidified with 1 N sulfuric acid. Table 5 characterizes the most typical experiments.

Table 5 shows that the reaction rate at −41°C. is higher than the normal rate (corresponding to an established constant) at +20°C., i.e., at a low temperature we have quite another process. Curves on figure 3 give a graphical illustration of these reactions.

Plotting values of ln K against $1/T$ (figure 1) we obtain a straight line. The low activation energy, 7000 calories (notwithstanding the abnormally small value of the coefficient A of the Arrhenius equation, 5.2×10^5), indicates the facility with which the process takes place. This is also shown by the high values of the velocity constants: the calculation of the velocity constants at 20°C. using the values at these low temperatures gives the value 3.1. Thus the presence of two stages in the interaction between peracid and aldehyde cannot be doubted.

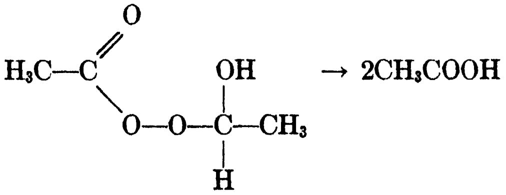
D. The mechanism of the reaction and the method for the quantitative determination of the intermediate stage

The intermediate product which is here formed might be thought of as a direct addition product of a molecule of peracid to a molecule of aldehyde according to the scheme:



(a)

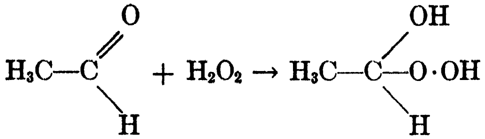
forming a new peroxide compound, hydroxyethylacetyl peroxide. The peroxide intermediate product shown in scheme a slowly decomposes, forming 2 molecules of acetic acid



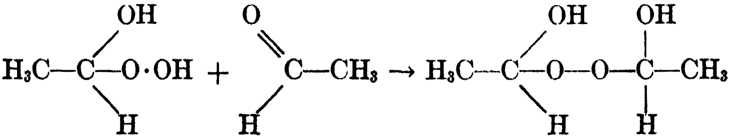
(b)

In the course of the process b, the equilibrium in a is shifted to the right, and thus the reaction rate in a is determined by the reaction rate of the second stage (b).

The possibility of the formation of such a peroxide intermediate compound by the interaction of peracid with aldehyde was pointed out by Wieland (5). He was, however, not able to demonstrate by direct experiments the formation of the addition product of peracetic acid with acetaldehyde, and traced the disappearance of the peracetic acid only in the aqueous solution of aldehyde. Hence Wieland inferred that the oxidation of aldehyde by the peracid is due to dehydrogenation of aldehyde hydrate. Wieland and B. Wingler (6) obtained a compound like (a) by the action of hydrogen peroxide on acetaldehyde. Rieche (4) describes such a compound obtained by the action of ethyl-hydroperoxide on aldehyde:



$$H_3C{-}\underset{H}{\overset{O}{C}} + H_2O_2 \rightarrow H_3C{-}\underset{H}{\overset{OH}{C}}{-}O{\cdot}OH$$



$$H_3C{-}\underset{H}{\overset{OH}{C}}{-}O{\cdot}OH + \underset{H}{\overset{O}{C}}{-}CH_3 \rightarrow H_3C{-}\underset{H}{\overset{OH}{C}}{-}O{-}O{-}\underset{H}{\overset{OH}{C}}{-}CH_3$$

We found the means of using the iodine evolved in the *neutral* potassium iodide solution (aqueous or methanol) for the determination of the whole amount of active oxygen contained in the peracetic acid and in the hydroxyethylacetyl peroxide. On the other hand, free peracetic acid may be determined in the acid solution of potassium iodide; under the action of the acid, the intermediate peroxide product is readily decomposed and the iodine evolved corresponds to the free peracetic acid only. Thus if the reaction is carried out at low temperatures and portions are introduced into a neutral potassium iodide solution, we are able to state that the amount of active oxygen remains practically unchanged throughout the experiment, so that it may seem that no process takes place at all. But when the same portions are brought into an acid solution of potassium iodide a gradual decrease of the amount of iodine evolved may be observed, which corresponds to the expenditure of peracetic acid for the formation of the intermediate peroxide product according to equation a.

The decomposition of the intermediate product according to equation b must be a monomolecular reaction, and this type of reaction is actually observed.

The data in table 6 may serve as an illustration for the above.

The experiments as well as other similar ones enable us to calculate the activation energy for the decomposition of the intermediate product. Thus, based on data of this experiment we find the latter to have a value of 18,800 calories, and from the data of another experiment 16,100. These values closely approach the values of the activation energy of the summary process of the reaction

$$CH_3COOOH + CH_3CHO \rightarrow 2CH_3COOH$$

at 10–30°C. shown in table 4 and amounting on the average to 16,000 calories.

Quite analogous data were also obtained in a chloroform solution. We were able also to demonstrate analytically the formation of the intermediate peroxide compound by preparing a highly concentrated solution of this compound. Owing to the interaction between acetaldehyde and peracetic acid in a toluene solution at −30°C., and the subsequent cooling of the solution down to −40°C., white crystals precipitated from the solution which could easily be separated from the mother liquor. These crystals readily melt at −20°C., forming a transparent liquid with a peroxide concentration 4.5 times higher than that of the solution decanted from the crystals.

TABLE 6

Formation of the intermediate product

$t = -40°C.$

TIME FROM THE BEGINNING IN MINUTES	PERACETIC ACID IN MOLES	
	Acid KI solution	Neutral KI solution
0	0.001946	0.001941
10	0.001305	0.001937
20	0.000903	0.001957
35	0.000601	0.001907

Decomposition of the intermediate product

TIME FROM THE BEGINNING IN MINUTES	INTERMEDIATE PRODUCT IN MOLES	K (sec $^{-1}$) × 10^5
	$t = +10°C.$	
0	0.001881	
20	0.001821	2.70
46	0.001748	2.62
81	0.001653	2.66
	$t = +20°C.$	
0	0.001204	
30	0.001034	8.43
82	0.000795	8.42
107	0.000697	8.38

Thus an addition product of acetaldehyde and peracid of a peroxide character actually seems to exist. In this manner the proposed scheme of the mechanism of the process is fully supported kinetically and analytically. The proposed method enables us to study each stage of this process separately.

II. KINETICS OF INTERACTION BETWEEN PERACETIC ACID AND OTHER ALDEHYDES

It was interesting to determine whether the proposed scheme holds for reactions with other aldehydes or whether the behavior of the acetaldehyde is specific.

For this purpose a series of preliminary experiments was started with isovaleraldehyde and peracetic acid. The kinetics of this reaction is quite analogous to that of the acetaldehyde reaction.

The results obtained show the same characteristic features as the reactions with acetaldehyde, a sharp inflection of the reaction velocity curve near the beginning indicating the existence of an intermediate stage going on with a considerably high rate even at −30°C. Thus we have reason to infer that the proposed mechanism of interaction between peracetic acid and acetaldehyde is characteristic for all aliphatic aldehydes.

The effect of water on the reaction rate between peracetic acid and acetaldehyde was also studied. We have found that the accelerating effect of water is connected with the acceleration of the second stage of this process, i.e., the decomposition of the intermediate peroxide. These experiments confirmed the proposed mechanism. Details of this work will be given in another paper.

III. SUMMARY

1. The kinetics of interaction between peracetic acid and acetaldehyde were studied in acetic acid, benzene, nitrobenzene, chloroform and toluene solution at temperatures varying between 10–30°C. The activation energy varied between 15,400 and 16,300 calories in various solvents.

2. It was found that the reaction follows the second-order equation, but in the beginning there is a short period of high reaction velocity, due to the intermediate stage.

3. A mechanism of the process is proposed according to which a peroxide compound (hydroxyethylacetyl peroxide) is formed as intermediate product.

4. A method for the quantitative determination of the intermediate peroxide in presence of peracetic acid is given.

5. Experiments were carried out with the purpose of obtaining (chiefly) the intermediate peroxide as a product of the reaction at temperatures between −40° and −60°C. The activation energy of this reaction amounts to 7000 calories. The coefficient A of the Arrhenius equation $K = Ae^{-E/RT}$ has the abnormally low value of 5.2×10^5.

6. A series of experiments was carried out in order to determine the kinetics of the monomolecular decomposition of the intermediate product.

7. The mechanism proposed was extended to other aliphatic aldehydes

by testing its applicability to the interaction of peracetic acid with isovaleraldehyde.

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THE CHLORINATION OF PROPANE. I

THE HOMOGENEOUS REACTION[1]

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The chlorination of the paraffin hydrocarbons has been the subject of many investigations. Most of the chlorination studies have been concerned with methane and natural gas in the hope of obtaining important and useful products. The literature resulting from these investigations has been well summarized by Egloff, Schaad, and Lowry (2). Much of the work to date has been qualitative in nature and there are many patents which claim to be able to produce any one of the substitution products by a variation in the conditions of the reaction. A good deal of study has also been devoted to the effect of different catalysts.

Since the quantitative side of the chlorination problem has been largely neglected it was felt that such a study from the standpoint of kinetics was highly desirable. The results obtained would be of theoretical interest in addition to possible practical applications. The latter results would be of particular value in this country, where such large quantities of the lower paraffin hydrocarbons are available.

The following investigations give the results of quantitative studies on the chlorination of propane. The work was divided into studies on the homogeneous and the heterogeneous reaction. Propane was chosen as the chlorine acceptor because (1) it is the simplest hydrocarbon having a secondary carbon atom, (2) it is the simplest paraffin hydrocarbon all of whose chlorinated products are liquids at room temperature, and (3) it is readily available in a state of high purity.

APPARATUS AND MATERIALS

The reacting gases were passed through purification trains, drying tubes, flowmeter, and mixing chambers before being admitted to the electrically heated reaction zone. The products were condensed in a trap placed in a salt–ice bath. The unused chlorine and the hydrogen chloride formed were absorbed in a solution of potassium iodide and the unused propane was collected in a gasometer. A by-pass system absorbed the chlorine and hydrogen chloride during the time the system was reaching a steady state.

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[1] The material here presented formed a part of thesis submitted to the Graduate Faculty of the University of Minnesota by Samuel Yuster in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1934.

[2] Shevlin Fellow, 1931-32.

Electrolytic chlorine was used throughout this investigation. It was found that chlorine from a fresh cylinder attacked the brass needle valve so that the rate of flow gradually decreased. The first chlorine was allowed to escape directly into a solution of sodium hydroxide for a short period of time. When this was done the rate of flow through the needle valve remained constant and no further trouble was experienced. Traces of water coming out with the first chlorine probably caused the difficulty.

Propane of a high grade was obtained in cylinders for use in this work. The purification train removed the unsaturated gases as well as those of an acidic character.

The Pyrex glass packing used in one of the runs was made by breaking scrap Pyrex and sieving. The 8 to 14 mesh fraction was used and cleaned with cleaning solution. It was washed with water, dried with alcohol and ether, and placed in the catalyst chamber.

METHOD OF OPERATION

At the beginning of a series of runs, the chamber was flamed while oxygen was slowly passed through it. The oxygen was then swept out with nitrogen.

The temperature of the furnace was set by means of the lamp bank and the rate of flow of the gases adjusted by means of the flowmeters. During this adjusting period the gases were passed through the by-pass system.

When a steady state had been reached, the necessary stopcock was turned so that the gases passed through the potassium iodide absorption train, where the unused chlorine and the hydrogen chloride formed were absorbed. The unused propane passed into a gas-collecting bottle, where it displaced an equal volume of water.

The flowmeter readings, chamber temperature, room temperature, duration of run, and the barometric pressure were recorded for a given run. The amount of water displaced by the unused propane was weighed and the volume of gas corrected to standard conditions. The potassium iodide solution was removed from the absorbers, and the iodine and hydrochloric acid content determined respectively with standard thiosulfate and alkali.

METHOD OF CALCULATION

In a normal chlorination, one molecule of hydrogen chloride is formed for each chlorine molecule used regardless of the mechanism of chlorination.

(cc. of sodium thiosulfate) × normality factor × 11.2 = cc. of chlorine unused. (cc. of potassium hydroxide) × normality factor × 22.4 = cc. of chlorine used. The sum of these two quantities will give the total chlorine admitted into the system. This should agree with the setting of the chlorine flowmeter if the reaction is behaving in a normal manner. The amount of chlorine used divided by the total chlorine input multiplied by 100 gives the per cent of chlorine used.

DISCUSSION OF RESULTS

Errors

The greatest difficulty encountered in this research was met in duplicating results. Since the slightest trace of oxygen inhibited the reaction even though the rate of flow and temperature were carefully controlled, check results were difficult to obtain. Despite the fact that the walls were flamed at the beginning of each series, the first measurements had to be discarded because of the extreme activity of the wall. After use, this catalytic effect reached a steady state and the results were more consistent.

The reaction was also diminished by the adsorption of chlorinated propanes by the wall. These adsorbed products were further acted upon by chlorine, became less volatile, and thus decreased their possibilities of escape. The rate of the reaction progressively decreased until the whole surface was covered with these poisoning agents. In these experiments, it was found that this autopoisoning was greatest at the higher temperatures and high chlorine to propane ratios.

In order to minimize these disturbing factors, the runs were made as rapidly as possible, but time was allowed for equilibrium to establish itself. The reactants were not allowed to remain in the reaction zone when the apparatus was not in use. They were swept out with nitrogen.

The rates of flow used in these series were 2, 10, 20, and 50 liters of reactants per hour. Since the volume of the reaction chamber was 100 ml., the space velocity, or the volume of gas passing through unit volume of the reaction zone in unit time, may be obtained by dividing the rate of flow in milliliters per minute by 100. For example, taking 10 liters per hour as the rate of flow:

$$\text{Space velocity} = \frac{\dfrac{10 \times 1000}{60}}{100} = 1.66$$

Then 1.66 of a volume of reactants pass through unit volume of reaction zone in one minute. Another way of stating it would be that on the average (disregarding adsorption, diffusion, convection currents, etc.) a given molecule would be in the reaction zone 0.6 of a minute.

Each rate of flow was divided into three series: runs in which the partial pressures of the reactants were equal, and runs in which the partial pressure of one of the reactants was twice that of the other. A series of runs was also made when the chamber was rinsed with a saturated solution of potassium chloride in an attempt to determine the effect of the wall.

Evidence from these experiments seemed to point to the fact that the so-called homogeneous gas phase chlorination of propane takes place by a chain mechanism. The reaction was inhibited by oxygen, an induction period was noticed when the reaction chamber walls were activated, explosions took place which are explained on the basis of branching chains, and a packed chamber cut down the extent of chlorination because of the decrease in the number of links in the chain.

The photochlorination of methane has been recently studied by Coehn and Cordes (1); they postulate a mechanism which is similar to that suggested in this problem. There are two possibilities to be considered, and the initial step in both cases would be the dissociation of a chlorine molecule into two chlorine atoms.

$$Cl_2 + \text{heat} \rightarrow Cl + Cl$$

This might take place in the gas phase owing to collisions, or on the wall because of some type of activated adsorption. The relative importance of the two processes is undoubtedly a function of the conditions.

The possible mechanisms for the chlorination of propane are given by the following equations:

Mechanism I.

$$\begin{array}{ll}
 & Cl + C_3H_8 \rightarrow C_3H_7Cl + H \\
 & H + Cl_2 \rightarrow HCl + Cl \\
(a) & Cl + C_3H_8 \rightarrow C_3H_7Cl + H \text{ etc.} \\
(b) & Cl + C_3H_7Cl \rightarrow C_3H_6Cl_2 + H \text{ etc.}
\end{array}$$

Mechanism II.

$$\begin{array}{ll}
 & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\
 & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \\
(a) & Cl + C_3H_8 \rightarrow C_3H_7 + HCl \text{ etc.} \\
(b) & C_3H_7Cl + Cl \rightarrow C_3H_6Cl + HCl \text{ etc.}
\end{array}$$

Since no thermal data could be obtained on the chlorination of propane, the corresponding data given by Coehn and Cordes (1) on methane were used to decide on the most probable mechanism.

Mechanism I.

$$\begin{array}{lr}
CH_4 + Cl_2 \rightarrow C_4H_3Cl + HCl & +\ 22{,}000 \text{ cals.} \\
H + Cl \rightarrow HCl & +100{,}000 \text{ cals.} \\
Cl + Cl \rightarrow Cl_2 & +\ 58{,}000 \text{ cals.} \\
\hline
CH_4 + Cl \rightarrow CH_3Cl + H & -\ 20{,}000 \text{ cals.}
\end{array}$$

Mechanism II.

$$\begin{array}{lr} CH_4 + \Delta \rightarrow CH_3 + H & -90{,}000 \text{ cals.} \\ H + Cl \rightarrow HCl & +100{,}000 \text{ cals.} \\ \hline CH_4 + Cl \rightarrow CH_3 + HCl & +10{,}000 \text{ cals.} \end{array}$$

It may be seen, therefore, that mechanism II is the more probable from a thermal standpoint. In addition, the presence of free radicals is required to explain the evidence obtained for coupling reactions. Since mechanism I requires the formation of hydrogen atoms, it would be expected that some of these atoms would combine to form hydrogen molecules. To test this, the gases were condensed in a liquid air trap after passing through the reaction zone. All possible gases except hydrogen should be condensed. No hydrogen was detected.

We shall, therefore, take as our most probable mechanism the following:

$$\begin{array}{ll} \text{(a)} & Cl_2 + \text{heat} \rightarrow Cl + Cl \\ & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \\ & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \text{ etc.} \\ \text{(b)} & C_3H_7Cl + Cl \rightarrow C_3H_6Cl + HCl \\ & C_3H_6Cl + Cl_2 \rightarrow C_3H_6Cl_2 + Cl \text{ etc.} \end{array}$$

Chain-breaking reactions:

$$\begin{array}{c} Cl + Cl \rightarrow Cl_2 \\ C_3H_7 + Cl \rightarrow C_3H_7Cl \\ C_3H_6Cl + Cl \rightarrow C_3H_6Cl_2 \\ C_3H_5Cl_2 + Cl \rightarrow C_3H_5Cl_3 \text{ etc.} \\ C_3H_7 + C_3H_6Cl \rightarrow C_3H_{13}Cl \\ \text{Active group} + O_2 \rightarrow \text{Inactive group.} \end{array}$$

All of the chain-breaking reactions require three body collisions in order to take place. The reactions are so exothermic that the resulting molecule will not exist as such unless some third body (either a third molecule or the wall) removes enough energy to leave a stable group.

The complete picture is not given in the above equations, as the complete chlorination of propane (if possible) is an eight-stage process with an enormous number of combinations in the intermediate stages. The probability of reaching the higher stages of chlorination drops off very rapidly, but undoubtedly they are reached to a small extent.

Under some conditions, in the empty chamber runs, explosions took place with the deposition of carbon. This could not be explained on the basis of the reaction

$$C_3H_8 + 4Cl_2 \rightarrow 3C + 8HCl$$

as the probability of four chlorine molecules and one propane molecule colliding simultaneously is practically nil. We must therefore postulate a series of degradation reactions similar to that given by Coehn and Cordes (1) for the production of carbon in the chlorination of methane.

$$C_3H_7 + Cl \rightarrow C_3H_6 + HCl$$
$$C_3H_6 + Cl \rightarrow C_3H_5 + HCl$$
$$C_3H_5 + Cl \rightarrow C_3H_4 + HCl \text{ etc.}$$

In the case of propane there may be splitting of the C—C bond to give a more simple molecule.

On the basis of the mechanism postulated for a one-stage process, calculations were made to determine the theoretical rate of reaction. A cubic equation was obtained for the concentration of the chlorine atoms, which made the solution hopeless. It is believed that too many factors varied to make the results valid for comparison with theory. Since the wall can both initiate and break chains, it is to be expected that the adsorption of chlorinated propanes should complicate matters. The reaction is bimolecular, but what the order should be, considering all the stages, is unknown.

TABLE 1

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE °C.	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
160	533	502	1	503	0.2
171	510	443	9	452	2.0
189	453	441	33	474	7.0
202	500	453	73	526	13.8
210	490	386	124	510	24.4
220	363	303	222	525	42.3
235	302	135	349	484	72.0
246	281	58	436	494	88.3
249	234	32	413	445	92.8
260	229	16	484	500	96.8
283	231		495	495	100.0

Figure 1, typical data of which is given in tables 1, 2, and 3, is a summary of the 2 liters per hour runs. Figure 2, a portion of which is shown in figure 1, shows the difficulty encountered in checking results. The points in this graph, a typical series of which is given in table 3, tend to diverge more and more from the average as the temperature rises. This series involved the use of a high partial pressure of chlorine. Both high temperatures and high chlorine content in the reactants favor the formation of higher chlorinated propanes. The poisoning of the wall under these conditions should also be greater. This was proved to be the case, since the chamber was found to be covered with a brownish substance after a series of runs. The curve in figure 2 represents one series of runs beginning with a clean chamber at low temperatures, followed by successive temperature increments.

TABLE 2

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
126	638	264	6	270	2.2
166	695	310	30	340	8.8
182	680	278	62	340	18.2
190	656	254	86	340	25.3
194	660	226	124	350	35.4
208	521	111	214	325	65.8
217	505	61	282	343	82.3
230	469	25	313	338	92.6
251	465	6	323	329	98.1

TABLE 3

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:2$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
171	345	675	2	677	0.3
185	368	658	11	669	1.6
197	352	554	35	589	5.9
212	280	574	107	681	15.7
222	231	425	215	640	33.6
231	163	262	415	677	61.3
238	173	184	505	689	73.2
245	126	170	415	628	72.9
258	140	203	451	654	69.0
266	141	181	457	638	71.6
275	97	51	596	647	92.1

An apparent negative temperature coefficient of reaction was found at the higher temperatures, which is not in harmony with chlorination reactions. It was thought that the phenomenon might be caused by a new type of reaction, but the effect was later proved to be due to poisoning. Poisoning at these higher temperatures was so rapid that there was apparently a negative temperature coefficient of reaction. After this poisoning reached a steady state a normal curve was obtained, but this was shifted along the temperature axis.

The ratio of chlorine to propane was varied in an attempt to determine the order of the reaction. It was realized that at least two effects would be involved in the determination of the extent of chlorination. The greater the partial pressure of chlorine in the reactants the more chlorine atoms are formed for the initiation of chains. However, a higher chlorine content would tend to produce higher chlorinated products which act as poisons. Because of these two effects, it should be expected that the extent of chlorination when plotted against the partial pressure of chlorine would go through a maximum. The type of curves represented in figure 1 should have the same relative position to one another no matter what the total rate of flow might be, providing the type of reaction taking place is not a function of the rate of passage of the reactants through the heated zone. A comparison of figures 1, 3, 4, and 5 shows that there was some change in the type of reaction with the rate of flow. This change was probably due to a change in the relative importance of chain initiation at the wall and in the gas phase. The complicating factor of explosions was introduced at the higher rates of flow. The decrease in reaction rate for an increase in the rate of flow, as shown by comparing figures 1 and 3, is to be expected.

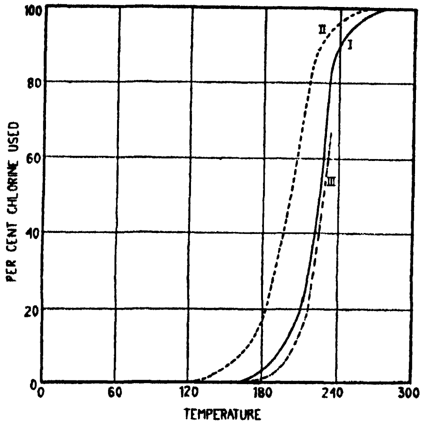

FIG. 1

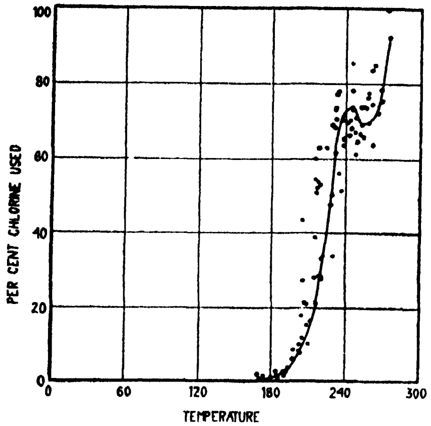

FIG. 2

FIG. 1. SUMMARY OF THE TWO LITERS PER HOUR RUNS

Curve I, $C_3H_8:Cl_2 = 1:1$; curve II, $C_3H_8:Cl_2 = 2:1$; curve III, $C_3H_8:Cl_2 = 1:2$

FIG. 2. EMPTY CHAMBER RUNS, SHOWING DIFFICULTY IN CHECKING RESULTS

Rate of flow, two liters per hour; $C_3H_8:Cl_2 = 1:2$

The large increase in rate of reaction in going from a 1:1 to a 1:2 ratio of propane to chlorine, using a total rate of flow of 2 liters per hour, does not compare very favorably with the corresponding result at 10 liters per hour, which only shows a small increase in rate.

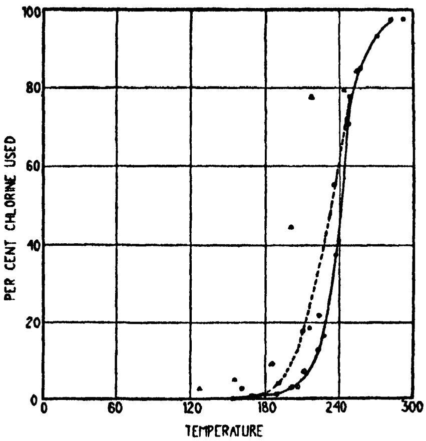

FIG. 3

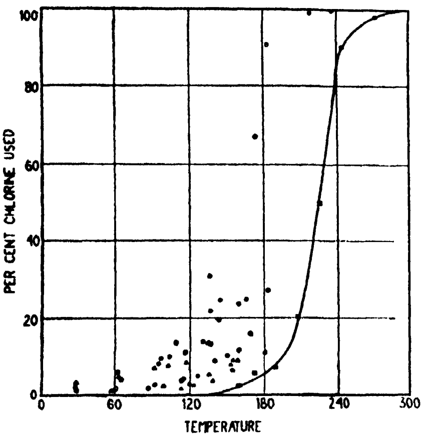

FIG. 4

FIG. 3. RESULTS OBTAINED IN EMPTY CHAMBER RUNS WITH RATE OF FLOW TEN LITERS PER HOUR

—⊙ $C_3H_8:Cl_2 = 1:1$
---⊡ $C_3H_8:Cl_2 = 2:1$
△ $C_3H_8:Cl_2 = 1:2$

FIG. 4. RESULTS OBTAINED IN EMPTY CHAMBER RUNS WITH RATE OF FLOW TWENTY LITERS PER HOUR

⊙ $C_3H_8:Cl_2 = 1:1$; ⊡ $C_3H_8:Cl_2 = 2:1$; △ $C_3H_8:Cl_2 = 1:2$

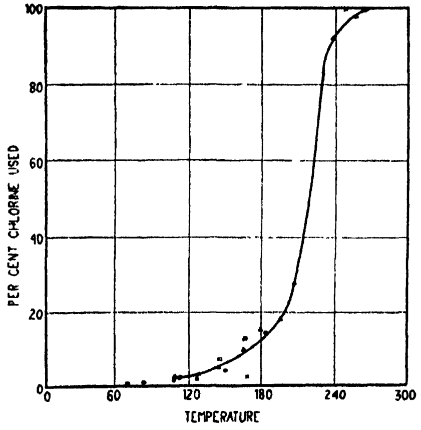

FIG. 5. RESULTS OBTAINED IN EMPTY CHAMBER RUNS WITH RATE OF FLOW FIFTY LITERS PER HOUR

⊙ $C_3H_8:Cl_2 = 1:1$; △ $C_3H_8:Cl_2 = 2:1$; ⊡ $C_3H_8:Cl_2 = 1:2$; × $C_3H_8:Cl_2 = 1:2$ (Pyrex-packed chamber).

Pease (3) has shown that a solution of potassium chloride when placed on the walls of a reaction chamber will inhibit certain reactions initiated at the wall. Since the changing activity of the wall was especially troublesome in this reaction, it was thought desirable to test the effect of potassium chloride. The chamber was washed with a saturated solution of potassium chloride and then flamed. The reactions were carried out in the usual way. Comparing the results with the corresponding data from an untreated chamber showed very little difference. In fact, the results might lead one to conclude that there was a very slight catalytic effect in the potassium chloride experiments. This was not very definite.

TABLE 4

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. C_3H_8:Cl_2 = 1:1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
154	311	308	1	309	0 1
190	344	328	5	333	1 5
201	344	322	11	333	3 3
212	334	308	24	332	7 2
228	319	282	56	338	16 5
238	305	220	131	351	37 4
248	247	98	238	336	70 8
259	191	47	266	313	84 9
284	154	8	321	329	97 6

TABLE 5

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. C_3H_8:Cl_2 = 2:1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
169	455	219	2	221	0.9
190	446	208	9	217	4 2
211	440	179	38	217	17.5
236	396	97	119	216	55.1
250	382	50	172	222	77.5
272	384	16	210	226	92.9
294	389	6	215	221	97.2

Explosions

Figures 3, 4, and 5 show the results obtained at higher rates of flow. It will be noted that runs involving high chlorine partial pressures are the

TABLE 6

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. C_3H_8:Cl_2 = 1:2

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
127	233	444	13	457	2.8
155	235	420	23	443	5.2
185	231	397	40	437	9.1
245	96	89	245	434	79.4
255	96	75	402	477	84.2
219	103	94	330	424	77.8
201	165	253	200	453	44.1

TABLE 7

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. C_3H_8:Cl_2 = 1:1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
28	404	393		393	
70	422	400	1	401	0.3
83	420	390	3	393	0.8
108	420	396	5	401	1.3
127	420	392	7	399	1.8
150	447	368	15	383	3.9
184	411	338	55	393	14.0

TABLE 8

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. C_3H_8:Cl_2 = 2.1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
108	542	269	7	276	2.5
128	546	264	9	273	3.3
144	544	258	13	271	4.8
165	536	244	26	270	9.6
179	535	230	40	270	14.7
196	518	232	49	281	17.4
207	522	195	74	269	27.5
239	426	23	253	276	91.5
258	415	7	268	275	97.4

least consistent. The two factors contributing to this are explosions and poisoning, which are favored by high chlorine partial pressures.

The explosions encountered in this research were never of the shattering type, as at no time were they strong enough to break the reaction chamber. The explosions were periodic and at 20 liters per hour total rate of flow, with a partial pressure of the chlorine of 0.5 atmosphere, they took place about every thirty seconds. At higher rates of flow, the explosions occurred more frequently.

The use of high partial pressures of propane seemed to eliminate the explosions. This would point to chlorine atoms as the initiators of the branching chains. With high partial pressures of chlorine, the explosions started at as low a temperature as 150°C. Using equal volumes of propane and chlorine, the temperature of initiation was about 190°C. In a few cases it was possible to "slip" past this temperature and proceed to higher temperatures without explosions. On dropping the temperature, explosions reappeared.

TABLE 9

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. C_3H_8:Cl_2 = 2:1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
112	287	519	15	534	2.8
145	281	493	34	527	6.5
167	270	472	66	538	12.3

Conditions same as above except chamber is packed with Pyrex

168	283	517	11	528	2.1
250					100.0

Runs were also made when the chamber was packed with broken Pyrex glass of 8–14 mesh (see figure 5 and table 9). These experiments were made with a high chlorine partial pressure, a condition which greatly favors explosions. Comparing the values obtained with the corresponding results in the unpacked chamber, a sixfold decrease in the extent of chlorination is found at the lower temperatures. Even with ten times the surface exposed for the activation of the chlorine, the chain-breaking effect of the wall outweighed the initiation of chains. No explosions were encountered at any time while operating over the whole temperature range. It might be reasoned that explosions are not evidence for a chain mechanism, as any exothermic reaction taking place in a thermally insulated chamber may utilize the heat of reaction to activate other molecules.

This autoactivation could give explosions. Part of the explosion is undoubtedly due to this phenomenon, but the formation of branching chains is probably the chief factor. A packing having a good heat conductivity would both shorten chains and conduct away the heat of reaction. From the standpoint of its property of transferring heat, Pyrex glass is not so very different from a gas. Nevertheless, the glass packing very effectively suppressed the explosions. Consequently, the explosions must have been stopped by the breaking of the chains.

Using the Arrhenius equation the heat of activation can be calculated.

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_2T_1}$$

k_2 and k_1 are the velocity constants at temperatures T_2 and T_1, E the heat of activation, and R, the gas constant, or

$$2.3 \log_{10} \frac{k_2}{k_1} = \frac{E}{R} \frac{T_2 - T_1}{T_2T_1}$$

Neither k_1 nor k_2 can be calculated, as the order of the reaction is not known. The rate equation for the single stage process is given by the equation

$$\frac{d(C_3H_7Cl)}{dt} = k(C_3H_8)^m(Cl_2)^n$$

Since m and n are not known, the above equation cannot be integrated to determine the velocity constant. The Arrhenius equation only requires a ratio of velocity constants at two temperatures and this can be obtained from the graphs.

Using the data from the experiments with a high partial pressure of propane, as given in figure 1, the following calculation was made. These data were chosen because a high partial pressure of propane minimized the poisoning of the walls.

The ratio k_2/k_1 is equal to 2 for the temperature range 184°C. to 199°C.

$$2.3 \log_{10} 2 = \frac{E}{2} \frac{472 - 457}{472 \times 457}$$

$$E = \frac{2 \times 2.3 \times 472 \times 457}{15} \log_{10} 2$$

$$E = 20{,}000 \text{ calories per mole of product formed}$$

If the data were to satisfy the Arrhenius equation over the whole temperature range, the curves would not be S-shaped but would become more and more vertical as the temperature increased.

It would be interesting to compare the energy of activation obtained from the temperature coefficient of reaction with the results from a calculation that assumes the chlorination to be of the simple bimolecular collision type. Since this reaction involves a chain mechanism, the energy of activation is undoubtedly composite, and it would be only fortuitous if any agreement was obtained by the two methods.

The equation for the collision theory is as follows:

$$N = N_0 e^{-\frac{E}{RT}}$$

where N = the number of effective collisions, N_0 = the total number of collisions, e = the natural logarithm base, R = the gas constant, T = the absolute temperature, and E = the energy of activation. N may be calculated from the data obtained from the extent of chlorination. The total number of collisions, N_0, is given by the formula:

$$\text{Collisions per cc. per sec.} = N_1 N_2 \sigma^2_{1,2} \sqrt{8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

N_1 and N_2 are the number of molecules of the two kinds per cubic centimeter, $\sigma_{1,2}$ is the mean of the molecular diameters, and M_1 and M_2 are the respective molecular weights.

According to figure 1 at 184°C. there was 20 per cent conversion of the chlorine to propyl chlorides. The partial pressures of the propane and chlorine were 0.667 atmosphere and 0.333 atmosphere, respectively. The number of molecules per cubic centimeter at the temperature T and partial pressure P would be given by the expression:

$$\frac{6.06 \times 10^{23} \times 273 \times P}{22{,}412 \times T}$$

Substituting our values:

$$\frac{6.06 \times 10^{23} \times 273 \times 0.667}{22{,}412\ (184 + 273)} = 1.085 \times 10^{19} \text{ molecules of } C_3H_8 \text{ per cc.}$$

$$\frac{6.06 \times 10^{23} \times 273 \times 0.333}{22{,}412\ (184 + 273)} = 0.543 \times 10^{19} \text{ molecules of } Cl_2 \text{ per cc.}$$

The diameter of the chlorine molecule as given by Rankine (8) is 3.2×10^{-8} cm. The diameter of the propane molecule given by Titani (9) is 4.16×10^{-8} cm. Substituting the proper values:

$$\text{Collisions per cc. per sec.} = 1.085 \times 10^{19} \times 0.543 \times 10^{19} \times$$

$$\left(\frac{3.2 \times 10^{-8} + 4.16 \times 10^{-8}}{2}\right)^2 \sqrt{8 \times 3.1416 \times 8.136 \times 10^7 \times 457\left(\frac{1}{71} + \frac{1}{44}\right)}$$

$$\text{collisions per cc. per sec.} = 4.68 \times 10^{28}$$

The chamber had a volume of 100 cc. and the rate of flow was 2000/3600 = 0.555 cc. per second (2 liters per hour). Therefore, the gas remained, on the average, 100/0.555 = 180 seconds in the heating zone.

The number of collisions taking place in the reaction zone per cubic centimeter during the 180 seconds of contact is $180 \times 4.68 \times 10^{28} = 8.42 \times 10^{30}$. Only 20 per cent of the chlorine was converted in the cubic centimeter or $\frac{0.543 \times 10^{19}}{5} = 1.08 \times 10^{18}$ collisions were effective. Substituting in our equation:

$$N = N_0 \, e^{-\frac{E}{RT}}$$

$$1.08 \times 10^{18} = 8.42 \times 10^{30} \, e^{-\frac{E}{2 \times 457}}$$

$$E = 27{,}000 \text{ calories per mole}$$

This is in fair agreement with the value of 20,000 calories obtained from the Arrhenius equation. Whether this has any significance is not known. Pease and Walz (7) obtained a similar agreement in their calculation on the chlorination of methane.

Since the formation of atomic chlorine is essential to the reaction, it would be interesting to calculate the length of the chains, presupposing that all of the chlorine atoms were formed in the gas phase by thermal dissociation.

The affinity of the reaction

$$\frac{1}{2}\, Cl_2(g) \rightarrow Cl(g)$$

is given by the expression (5):

$$A = 3500 - 1.37T \ln T + 0.0025T^2 - 1.5T$$

At the temperature 457° absolute we have

$$A = 3500 - 1.37 \times 457 \ln 457 + 0.00025\,(457)^2 - 1.5 \times 457$$
$$A = 30{,}000 \text{ calories}$$
$$A = -RT \ln K = -RT \ln \frac{(Cl)}{(Cl_2)^{1/2}}$$

The partial pressure of the chlorine was 0.333 atmosphere and using this value the concentration of the chlorine atoms at 457° absolute may be calculated.

$$30{,}000 = -2 \times 457 \ln \frac{(Cl)}{(0.333)^{1/2}}$$

$$(\mathrm{Cl}) = 5.49 \times 10^{-14} \text{ atmospheres}$$

$$(\mathrm{Cl}) = \frac{6.06 \times 10^{23} \times 5.49 \times 10^{-14} \times 273}{22{,}412 \times 457} = 8.87 \times 10^{5} \text{ atoms per cc.}$$

The rate of combination of the chlorine atoms at the equilibrium concentration would be given by the expression

$$\text{Collisions per cc. per sec.} = N^2\sigma^2 \sqrt{\frac{4\pi RT}{M}}$$

where σ in this case is the diameter of the chlorine atom. Since the value of this is unknown, the diameter of argon, 2.46×10^{-8} cm., will be used as an approximation. The above calculation also presupposes that every time two chlorine atoms collide a chlorine molecule is formed.

$$Z = (8.87 \times 10^{5})^2(2.56 \times 10^{-8})^2 \sqrt{\frac{4 \times 3.1416 \times 8.136 \times 10^{7} \times 457}{35.5}}$$

$Z = 59$ chlorine molecules formed per second per cubic centimeter

Since, at equilibrium, the rate of combination equals the rate of formation, then 59 chlorine molecules decompose per second per cubic centimeter to form 118 chlorine atoms. The gas remains in the reaction zone for 180 seconds, therefore 21,200 chlorine atoms will form in that time.

From our previous calculation, 1.08×10^{18} chlorine atoms reacted in this same period of time. The 21,200 chlorine atoms initiated all of the reaction, which indicates that a chain has approximately 10^{14} links. This value seems beyond reason. The photochemical combination of hydrogen and chlorine only gives a chain length of 1.4×10^{5} molecules per quanta (3).

Two suppositions were involved in this calculation: first, that every collision between chlorine atoms results in a combination; and second, that no chlorine atoms are formed at the wall. The probability of the first taking place is not known, but the true situation would probably give a shorter chain. Any activated adsorption of chlorine on the walls would produce chlorine atoms which if included in the calculation would also shorten the chains. The magnitude of the result in the calculation would indicate that it is considerable.

Product

High partial pressures of chlorine favored the formation of the higher chloro derivatives. High rates of flow in which the chlorine conversion was high gave higher chlorinated propanes than did lower rates of flow under similar conditions. This was probably due to the problem of the greater amount of heat to be dissipated at the higher rates of flow. As high as 75 per cent of the product was monochloropropane when a high propane partial pressure was used coupled with a low space velocity. The conversion under these conditions was between 80 and 90 per cent of the chlorine input.

SUMMARY

1. The homogeneous reaction of propane with chlorine has been studied.

2. The reaction was shown to be of the chain type, as evidenced by an induction period, inhibitory effect of oxygen, reduction in rate by packing and explosions.

3. The type of reaction was shown to change with change in rate of flow.

4. A mechanism has been postulated which seems to satisfy the peculiarities of the reaction.

5. It was shown that chains were both initiated and stopped by the wall.

6. High partial pressures of chlorine cause the wall to be poisoned.

7. Explosions were favored by high rates of flow and high partial pressures of chlorine.

8. The heat of activation was calculated by means of the temperature coefficient and by collision efficiency; fair agreement was obtained between the two values, which were about 20,000 calories per mole.

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LIQUID AMMONIA AS A SOLVENT. IV

ACTIVITIES OF AMMONIUM NITRATE, IODIDE, BROMIDE, AND CHLORIDE AT 25°C.

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The activities of solid non-volatile solutes in liquid ammonia may be obtained by measuring the vapor pressures of their solutions at various concentrations. Vapor pressure data also furnish an excellent means of testing the theories of concentrated solutions, since the measurements can be made over a very wide range of concentration.

The vapor pressure data used in this paper have been reported in a previous article (3). The values used in calculating the activities were taken from a smooth mole ratio versus vapor pressure curve. Ammonia gas deviates considerably from the behavior of an ideal gas; therefore the fugacity rather than the vapor pressure must be used in calculating the activities and showing deviations from Raoult's law. The fugacity was calculated from the vapor pressure using the equation (5)

$$\ln f = \ln P - \int_0^P \frac{\alpha}{RT}\, dP \qquad (1)$$

f is the fugacity, P is the vapor pressure, and

$$\frac{\alpha}{RT} = \frac{1}{P}\left(1 - \frac{PV}{RT}\right) \qquad (2)$$

The last term in equation 1 was evaluated from the known data for ammonia gas at 25°C. (4), using the equation

$$PV = RT + aP + bP^2 \qquad (3)$$

a and b are constants. This equation becomes

$$\frac{1}{P}\left(1 - \frac{PV}{RT}\right) = -A - BP = \frac{\alpha}{RT} \qquad (4)$$

---

[1] This paper is a part of a thesis submitted by W. E. Larsen to the Faculty of Purdie University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

or

$$2.3026 \log \frac{f}{P} = AP + \frac{BP^2}{2} \tag{5}$$

A and B (P in cm.) were found to be -1.356×10^{-4} and -2.578×10^{-8}, respectively.

The relationship $a_1 = f/f_0$ gives the activities of the solvent, f_0 being the fugacity of liquid ammonia, and f the fugacity of the solution. Our value of the vapor pressure, although lower than that reported by Cragoe (1), was used in calculating the fugacity of liquid ammonia, because our manometer gives the same per cent lower value for the vapor pressures of the solutions.

The activity of the solute was calculated from that of the solvent by equations resulting from the Gibbs-Duhem equation, namely,

$$\mathrm{d} \ln a_2 = -\frac{N_1}{N_2} \mathrm{d} \ln a_1 \tag{6}$$

a_2 is the activity of the solute, and N_1 and N_2 the mole fraction of the solvent and solute, respectively. Upon integrating and changing to common logarithms

$$\log \frac{a_2}{a_2'} = -\int_{a_1'}^{a_1} \frac{N_1}{N_2} \mathrm{d} \ln a_1 \tag{7}$$

The value of the integral was obtained by a graphical method. Measurements could not be made for solutions dilute enough to allow extrapolation to infinite dilution; consequently this method gave only relative activities. This necessitated giving an arbitrary value to a_2' at some concentration used as a reference point. A concentration of 1 molal was chosen as the reference point. This arbitrary assumption amounts to placing $a = 1$ at 1 molal, and consequently $\log a_2' = 0$; then by measuring the area between this point and any other point we have

$$\log ka_2 = -\text{ area} \tag{8}$$

Using this equation a series of values was obtained proportional to the activity. Assuming that the ammonium salts dissociate into two ions, the relative mean ionic activity coefficient is given by

$$k'\gamma = \frac{ka_2^{1/2}}{M} \tag{9}$$

M is the molality.

This series of $k'\gamma$ values is plotted against the molality in figure 1, which brings out the differences between the ammonium halides.

TABLE 1

$k'\gamma$ for ammonium nitrate

M	P	f	a	$k'\gamma$
	cm. Hg			
48.9	86.3	85.3	0.1270	1.17
42.8	103.2	101.8	0.1512	1.20
34.5	138.5	135.9	0.2019	1.19
27.2	187.4	182.6	0.2713	1.14
22.8	235.8	228.2	0.3391	1.05
18.9	292.7	281.0	0.4175	0.936
15.2	373.8	354.7	0.5270	0.779
11.2	489.1	456.3	0.6779	0.601
8.63	572.0	527.1	0.7831	0.510
6.38	643.8	586.8	0.8719	0.452
4.19	692.0	626.1	0.9303	0.483
2.94	713.6	643.5	0.9562	0.550
1.97	726.5	653.9	0.9715	0.677
1.40	733.4	659.4	0.9797	0.825
1.14	736.6	661.9	0.9835	0.930
0.917	739.2	664.0	0.9866	1.05
0.683	742.0	666.2	0.9899	1.25
0.508	744.0	667.8	0.9923	1.49
0.411	745.1	668.7	0.9936	1.69
Pure NH_3	750.6	673.0	1.0000	

TABLE 2

$k'\gamma$ for ammonium iodide

M	P	f	a	$k'\gamma$
	cm. Hg			
25.4	73.8	73.1	0.1086	11.5
22.6	98.0	96.7	0.1437	9.14
18.0	160.0	156.5	0.2325	5.66
16.4	195.7	190.5	0.2830	4.45
14.3	263.0	253.6	0.3767	2.96
12.0	360.0	342.3	0.5086	1.81
9.32	475.8	444.8	0.6609	1.13
6.45	598.8	549.5	0.8165	0.743
5.21	640.4	584.0	0.8678	0.676
4.19	671.3	609.3	0.9054	0.645
3.19	697.5	630.6	0.9369	0.644
2.20	717.9	647.0	0.9613	0.706
1.33	732.1	658.3	0.9782	0.869
1.07	736.0	661.5	0.9828	0.966
0.883	738.8	663.7	0.9861	1.06
0.675	741.7	666.0	0.9895	1.21
0.521	743.5	667.4	0.9917	1.41
0.399	745.1	668.7	0.9936	1.63
0.309	746.3	669.6	0.9950	1.87

TABLE 3

k′γ for ammonium bromide

M	P	f	a	$k'\gamma$
	cm. Hg			
24.8	162.0	158.4	0.2354	1.26
21.3	221.3	214.6	0.3189	0.993
17.3	319.7	305.7	0.4543	0.714
13.5	446.1	418.8	0.6223	0.500
10.5	550.4	508.8	0.7560	0.401
7.70	634.2	578.9	0.8602	0.360
5.23	688.2	623.1	0.9258	0.380
3.40	714.8	644.5	0.9576	0.464
2.39	725.4	653.0	0.9702	0.577
1.78	731.6	658.0	0.9776	0.696
1.28	736.9	662.2	0.9839	0.857
0.979	740.0	664.6	0.9875	1.01
0.766	742.1	666.3	0.9900	1.19
0.587	743.8	667.7	0.9920	1.42
0.455	745.1	668.7	0.9936	1.68
0.369	745.9	669.3	0.9945	1.93
0.280	747.3	670.4	0.9961	2.19

TABLE 4

k′γ for ammonium chloride

M	P	f	a	$k'\gamma$
	cm. Hg			
24.4	314.0	300.5	0.4465	0.239
21.8	379.0	359.4	0.5339	0.213
18.9	453.0	424.9	0.6313	0.192
16.3	525.0	487.2	0.7239	0.177
13.7	591.8	543.7	0.8079	0.171
10.7	653.4	594.7	0.8836	0.176
8.76	684.3	619.9	0.9211	0.190
7.40	700.0	632.6	0.9399	0.209
5.49	717.3	646.5	0.9606	0.255
4.00	727.1	654.4	0.9723	0.324
2.61	733.9	659.8	0.9803	0.462
1.96	737.2	662.4	0.9842	0.585
1.47	739.7	664.4	0.9872	0.740
1.06	742.2	666.4	0.9901	0.958
0.850	743.4	667.4	0.9916	1.14
0.667	744.6	668.3	0.9930	1.38
0.506	745.9	669.3	0.9945	1.63
0.390	747.7	670.8	0.9966	1.89

The method of Randall and White, if it could be used, would give absolute activities. Although their method has been used successfully for aqueous solutions by Pearce and Nelson (6), the extrapolation involved in the case of liquid ammonia is much more difficult. Their method was used to give an approximate value of the activity coefficient. Using these activity coefficients the value of k' for each concentration of the more exact series was obtained. These values of k' vary within the maximum limits of 0.65 per cent, showing that the two methods run parallel to a reasonable extent. The fact that k' is constant does not mean that the extrapolation is necessarily correct, but only that the two methods run parallel. The average value of k' for ammonium nitrate is 37.7, ammonium iodide 31.8, ammonium bromide 50.6, and ammonium chloride 83.5. These values show that the activities of these salts are low in liquid ammonia.

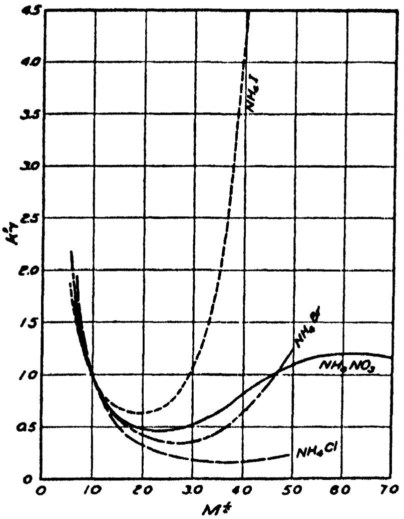

FIG. 1

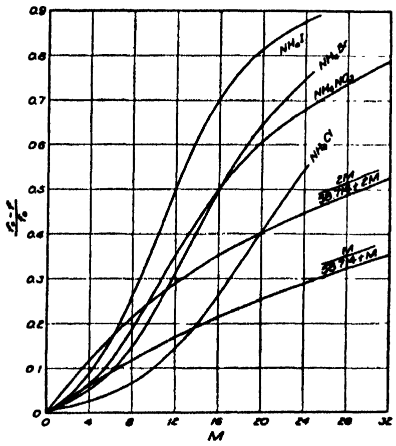

FIG. 2

FIG. 1. VALUES OF $k'\gamma$
FIG. 2. DEVIATIONS FROM RAOULT'S LAW

DEVIATIONS FROM RAOULT'S LAW

If the vapor is not ideal and the solute is a non-electrolyte, the fugacity depends on the concentration in the following manner;

$$f = f_0 N_1 \tag{10}$$

or

$$\frac{f_0 - f}{f_0} = N_2 = \frac{M}{58.71 + M} \tag{11}$$

The left side of equation 11 is really the fractional lowering of the fugacity.

If we consider that binary salts, such as the ammonium salts, are 100 per cent ionized, and that the ions resulting still behave as ideal solutes, then a relation similar to equation 11 is

$$\frac{f_0 - f}{f_0} = \frac{2M}{58.71 + 2M} \tag{12}$$

The deviations from the ideal are shown in figure 2, where two of the curves were made by plotting the right-hand side of equations 11 and 12 against the molality, and the others were made by plotting the fractional lowering of the fugacity against the molality. These solutions do not behave as ideal solutions either in the dilute or concentrated region. Such deviations in the concentrated region are not unexpected, but the trends of these curves in the dilute solutions are more unusual, since all but ammonium iodide show a smaller lowering of the fugacity than is predicted for a non-electrolyte. This effect is most marked for ammonium chloride, which does not cross the non-electrolyte curve until above 12 molal.

The interpretation of these results may be made from several viewpoints, as Hepburn (2) has shown. A possible explanation is that some form of association takes place, thus lowering the mole fraction of the solute. The relative positions of the curves for the different halides are what would be expected from this explanation.

The results in the concentrated region indicate that some of the solvent molecules have lost their fugacity, which may mean that they are attached to some of the solute ions. Although the solvation per ion is greater in the dilute solution, in the concentrated solution the number of solvent molecules that are bound up comprises a significant part of the total present, and the mole fraction of the solute increases faster than it otherwise would. The extent of solvation indicated makes it appear probable that both anion and cation are highly solvated.

SUMMARY

1. From the vapor pressures of solutions of ammonium nitrate, iodide, bromide, and chloride a quantity $k'\gamma$ has been calculated using the Gibbs-Duhem equation, and a plausible value of k' determined using the method of Randall and White.

2. The deviations from Raoult's law are shown, and it is suggested that these deviations can be explained if the solutes are partially associated, and there is considerable solvation between the ions resulting and the molecules of the solvent.

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THE RÔLE OF ORTHO SUBSTITUTION IN THE IONIZATION OF ORGANIC ACIDS AND BASES

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The conclusions of Smallwood (14) that the increase in acidity of ortho halogen-substituted acids over that of benzoic acid was due primarily to restricted rotation of the carboxyl group suggests that groups which have a depressing effect upon the ionization of aliphatic acids and meta and para substituted benzoic acids should produce an increased acidity in the corresponding ortho substituted benzoic acids.

Groups having low dipole moments and having little effect on the acidity of aliphatic acids are to be desired for a study of restricted rotation, in order to reduce internal electronic disturbances to a minimum. Methyl and ethyl groups fill these requirements. Table 1 shows the effect of ortho substitution on the dissociation constants of benzoic acids, based on the data of Scudder (13).

DISCUSSION

As predicted, the *m*- and *p*-toluic acids are weaker than benzoic acid. On the assumption that rotation is unrestricted, *o*-toluic acid should be weaker than benzoic acid; actually the ortho acid is stronger than the unsubstituted acid. *o*-Ethylbenzoic acid is also stronger than benzoic acid itself, and slightly more acidic than *o*-toluic acid. In the case of the dimethyl substituted benzoic acids, it is again evident that a methyl group in the ortho position is the primary cause for the increase in acidity, since the 3,5-dimethyl derivative is weaker and the 2,4- and the 2,5-dimethyl derivatives are stronger than benzoic acid. The trimethyl and tetramethyl derivatives also show that methyl groups in the ortho positions more than overcome the usual depressing effect of methyl groups in the meta and para positions. When both ortho positions are filled, the acidity of the resulting compound is greater than that in which but one ortho group is substituted.

It is known that the methoxyl and the ethoxyl groups have a slight acidifying effect upon substituted aliphatic acids. If the evidence presented by measurement of dipole moments is correct (6), substitution of these groups in the ortho position should cause no appreciable increase in acidity because they should not restrict rotation of the carboxyl group. The data for the methoxyl and ethoxyl derivatives shown in table 1 are in agreement with this assumption.

The evidence in favor of restricted rotation presented by the alkoxyl derivatives is less convincing because of the possibilities for molecular resonance (17), which would tend to have a decreasing effect upon acidity. However, if molecular resonance occurs in the toluic acids, the ortho acid would be weaker than the meta and para acids. Since *o*-toluic acid is stronger than either *m*- or *p*-toluic acid, the primary effect cannot be due to molecular resonance.

TABLE 1

Effect of ortho substituents on the dissociation constants of substituted benzoic acids

ACIDS	$K_{25°}$
Benzoic acid	6.6×10^{-5}
o-Toluic acid	1.37×10^{-4}
m-Toluic acid	5.8×10^{-5}
p-Toluic acid	4.3×10^{-5}
o-Ethylbenzoic acid	1.7×10^{-4}
3,5-Dimethylbenzoic acid	4.8×10^{-5}
2,4-Dimethylbenzoic acid	9.0×10^{-5}
2,5-Dimethylbenzoic acid	1.2×10^{-4}
2,4,6-Trimethylbenzoic acid	3.8×10^{-4}
2,3,5,6-Tetramethylbenzoic acid	3.0×10^{-4}
2,3,4,6-Tetramethylbenzoic acid	1.0×10^{-4}
2,3,4,5-Tetramethylbenzoic acid	6.5×10^{-5}
2-Methoxy-5-methylbenzoic acid	6.8×10^{-5}
2-Methoxy-4-methylbenzoic acid	4.1×10^{-5}
4-Methoxy-2-methylbenzoic acid	5.4×10^{-5}
2-Methoxybenzoic acid	8.2×10^{-5}
o-Ethoxybenzoic acid	7.2×10^{-5}
m-Ethoxybenzoic acid	9.2×10^{-5}
p-Ethoxybenzoic acid	5.1×10^{-5}

Pauling (12) has mentioned, in connection with molecular resonance, that bond energy is independent of orientation and that there will be free rotation about a single bond except in so far as rotation is hindered by steric effects arising from interactions of the substituent atoms or groups.

While both optical isomers of the free acid of the benzenesulfonyl derivative of 8-nitro-1-naphthylglycine, as well as their brucine salts, show mutarotation (11), it is not necessary that the di-ortho-substituted benzoic acids have the carboxyl group restricted to the extent necessary to produce optical isomerism. Several attempts to isolate optical isomers have resulted in failure: Lewkowitsch (9) failed to obtain optically active or mutarotatory 1-methyl-6-nitrobenzoic acid, and Adams and coworkers (7, 10) failed to isolate optically active di-ortho-substituted benzoic esters and diphenyl ketones. Following the usage of Betti (2), it would perhaps be better to use the term "diminished free rotation" in place of "restricted rotation," since the latter connotes optical activity. The diminished free rotation of the carboxyl group would be similar to the type occurring in 1,2-dichloroethane (15).

TABLE 2

The effect of ortho substituents on the dissociation constants of bases

BASE	$K_{25°}$
Aniline	3.8×10^{-10}
o-Toluidine	2.5×10^{-10}
m-Toluidine	4.9×10^{-10}
p-Toluidine	1.3×10^{-9}
N-Methylaniline	7.1×10^{-10}
N-Methyl-*o*-toluidine	3.9×10^{-10}
N-Methyl-*m*-toluidine	8.7×10^{-10}
N-Methyl-*p*-toluidine	2.1×10^{-9}
N-Ethylaniline	1.3×10^{-9}
N-Ethyl-*o*-toluidine	8.5×10^{-10}
N-Ethyl-*p*-toluidine	4.7×10^{-9}
N-Dimethylaniline	1.1×10^{-9}
N-Dimethyl-*o*-toluidine	7.3×10^{-9}
N-Dimethyl-*m*-toluidine	1.7×10^{-9}
N-Dimethyl-*p*-toluidine	3.2×10^{-9}
N-Diethylaniline	3.8×10^{-8}
N-Diethyl-*o*-toluidine	1.5×10^{-7}
N-Diethyl-*p*-toluidine	1.2×10^{-7}
Quinoline	6.3×10^{-10}
2-Methylquinoline	2.6×10^{-9}
Pyridine	2.3×10^{-9}
2-Methylpyridine	3.2×10^{-8}
2,6-Dimethylpyridine	1.0×10^{-7}
2,4,6-Trimethylpyridine	1.2×10^{-7}

Since substitution which causes increased acidity in organic acids usually leads to decreased basicity of organic bases, one would expect the *o*-toluidines to be less basic than aniline, which, in turn, should be less basic than the *m*- and *p*-toluidines. The expectation that ortho substitution leads to a decrease in the dissociation constants of organic bases (5) is borne out by the data presented in table 2.

The *N*-dimethyl and *N*-diethyl derivatives of aniline and substituted anilines fail to show the expected decrease in basicity. An explanation for this fact is that the introduction of two alkyl groups on the nitrogen causes a partial restriction of rotation such that further substitution in the ortho position has no further restricting effect. An instance similar to this, in the dimethyl and diethyl substituted malonic and glutaric acids, has been explained by Gane and Ingold (4), who suggest that an unexpected increase in acidity was caused by valency deflection, in addition to restricted rotation.

Within recent years a number of examples of retardation of chemical reactions by the presence of ortho substituents have been recorded (1). The question arises: Is the increase in acidity of acids or decrease in basicity of bases due merely to steric hindrance, or to diminished free rotation? It is possible that it may be due to both. In the quinolines, the nitrogen in the ring is not free to rotate. If substitution in the ortho position of quinolines causes steric hindrance, the resulting bases should be affected to about the same degree as are the *o*-toluidines. The data in table 2 show that ortho substituted quinoline and the ortho substituted pyridines are more basic than the parent substances, just the inverse of that noted for the *o*-toluidines. Therefore steric effect is excluded.

A similar case arises with the phenols, where the functional group contains only one atom attached to the oxygen. *o*-Cresol ($Ka = 6.3 \times 10^{-11}$) is weaker (8) than phenol ($Ka = 7.3 \times 10^{-11}$). This fact is also in accordance with the theory of restricted rotation and opposed to that of steric effect.

These results support the contention that diminished rotation of the functional group occurs in the ortho substituted benzoic acids and anilines. It must be borne in mind, however, that diminished free rotation cannot be measured quantitatively as yet, because there are very probably internal electronic disturbances accompanying diminished free rotation and incapable of being distinguished from it.

SUMMARY

Provisionally, the increase in acidity of ortho substituted benzoic acids and anilines has been attributed to the spacial proximity of the alphyl ortho substituent to the functional group to such an extent that there is diminished free rotation of the latter.

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THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID IN VARIOUS SALT SOLUTIONS[1, 2]

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In the previous paper (10) the catalytic constant of the hydrogen ion ($k_{H_3O^+}$) in the hydrolysis of diethyl acetal was determined in aqueous solutions of nine solvent salts. With the determination of the temperature coefficient this reaction can now be employed to measure kinetically the hydrogen-ion concentration of suitable buffer solutions. This paper presents the determination of the dissociation constant of benzoic acid in the nine solvent salt solutions over a wide range of concentration.

EXPERIMENTAL PART

Suitable buffer solutions were made from benzoic acid and carbonate-free sodium hydroxide solution, and the purified salts were added. The experimental method was the same as that used in the previous paper. The hydrogen-ion concentration was calculated from the equation:

$$k_{\text{obsd.}}/k_{H_3O^+} = C_{H_3O^+}$$

where the value of $k_{H_3O^+}$ is that for the corresponding concentration of the electrolyte. The classical dissociation constant (K_c) was calculated from the $C_{H_3O^+}$ and the stoichiometric composition of the buffer solution.

Table 1 gives the results of the measurements with lithium chloride, and tables 2 and 3 summarize the results in the other salt solutions.

The results are presented graphically in figure 1. The wide variation in the dissociation constant of the acid in the different salt solutions is particularly striking. For example, at 1 molar electrolyte concentration the difference between the lowest and the highest values is over 100 per cent, the value in lithium chloride being 12.84 and that in sodium *p*-toluenesulfonate 5.47.

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[1] An abstract of this paper was presented at the Eighty-sixth Meeting of the American Chemical Society held at Chicago, September, 1933.

[2] Abstracted from the dissertation of Leonard C. Riesch presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[3] George Leib Harrison Fellow in Chemistry, 1933–34.

In order to analyze the differences further, the value of the ratio $f_{\mathrm{H}}f_{\mathrm{B}}/f_{\mathrm{HB}}$ was calculated from the equation:

$$K_a = K_c f_{\mathrm{H}}f_{\mathrm{B}}/f_{\mathrm{HB}} \qquad (1)$$

where K_a represents the thermodynamic dissociation constant. The value of K_a used by Kilpatrick and Chase (4), 6.31×10^{-5}, has recently been confirmed by accurate measurements by Brockman and Kilpatrick (1).

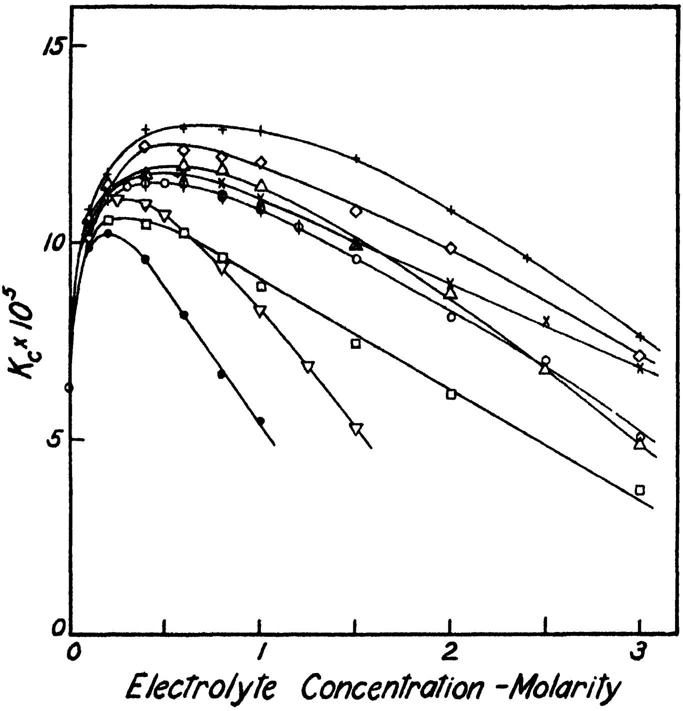

FIG. 1. ELECTROLYTE EFFECT ON THE DISSOCIATION CONSTANT OF BENZOIC ACID

○, KCl; △, NaCl; +, LiCl; □, $NaClO_4$; ◇, $LiNO_3$; ×, $NaNO_3$; ϕ, KNO_3; ▽, $C_6H_5SO_3Na$; ●, p-$C_6H_4(CH_3)SO_3Na$.

To obtain the mean activity coefficient of the ions of benzoic acid, $\sqrt{f_{\mathrm{H}}f_{\mathrm{B}}}$, f_{HB} was calculated from the equation

$$\log f_{\mathrm{HB}} = \beta C \qquad (2)$$

by using the experimental data in the literature. Table 4 gives the values of the "salting-out" constant.

In the case of the sulfonates the values were plotted from the data of Osol and Kilpatrick (9), and the activity coefficients were read from the plots. The values of $\sqrt{f_{\mathrm{H}}f_{\mathrm{B}}}$ are given in tables 5 and 6.

At 0.10 molar salt concentration the values of $\sqrt{f_{\mathrm{H}}f_{\mathrm{B}}}$ are the same within

2.5 per cent in the various salt solutions, while at 1, 2, and at 3 molar the maximum differences are 20, 25, and 40 per cent, respectively. The mean activity coefficient is greatest in sodium chloride solutions. The order for the chlorides and nitrates at high concentrations is Na > K > Li, and for the sodium salts the order for the anions is Cl > ClO_4 > NO_3 > sulfonates.

TABLE 1

The dissociation constant of benzoic acid in lithium chloride solutions at 25°C.

HB	LiCl + NaB	Λ OBSERVED	$C_{H_3O^+} \times 10^4$	$K_c \times 10^5$
moles per liter	*moles per liter*			
0.010	0.10	0.01794	2.040	10.83
0.010	0.20	0.02160	2.198	11.73
0.010	0.40	0.02828	2.402	12.90
0.010	0.60	0.03409	2.402	12.90
0.010	0.80	0.04030	2.398	12.87
0.010	1.00	0.04741	2.392	12.84
0.010	1.50	0.06770	2.277	12.18
0.005	2.00	0.04606	1.036	10.80
0.005	2.41	0.03025	0.4772	9.59
0.005	3.00	0.04025	0.3755	7.60

TABLE 2

The dissociation constant of benzoic acid in salt solutions at 25°C.

SALT + NaB	$K_c \times 10^5$			
	NaCl	KCl	$C_6H_5SO_3Na$	p-$C_6H_4(CH_3)SO_3Na$
moles per liter				
0.10	10.59	10.15	10.09	9.88
0.20	11.46	11.21	10.99	10.22
0.25			11.12	
0.30		11.41		
0.40	11.71		10.97	9.57
0.50		11.51	10.73	
0.60	11.94			8.18
0.80	11.85	11.20	9.39	6.63
1.00	11.40	10.88	8.27	5.47
1.25			6.84	
1.50	9.91	9.58	5.28	
2.00	8.71	8.11		
2.50	6.78	6.99		
3.00	4.85	5.04		

The other values for the dissociation constant of benzoic acid that are given in the literature are at 18°C. and 20°C., and it is probable that the change of the dissociation constant over this range of temperature is small.

This is borne out by the results of the determination of the temperature coefficient of the dissociation constant between 35°C. and 25°C. by the two-thermostat method. The results are summarized in table 7.

It is to be noted that, except for the values for 3 molar sodium chloride, the temperature coefficient in the various salt solutions is constant within approximately 3 per cent. From the average value 3.455, as compared with 3.395 for k_{35}/k_{25} for strong acids, it is evident that the temperature coefficient of the dissociation constant is small over this range.

TABLE 3

The dissociation constant of benzoic acid in salt solutions at 25°C.

SALT + NaB	$K_c \times 10^5$			
	$LiNO_3$	$NaNO_3$	KNO_3	$NaClO_4$
moles per liter				
0.10	10.21	10.43	10.35	10.43
0.20	11.28	11.31	11.10	10.87
0.40	12.46	11.71	11.48	10.47
0.60	12.32	11.73	11.49	10.24
0.80	12.16	11.52	11.14	9.63
1.00	12.02	11.15	10.83	8.88
1.20			10.41	
1.50	11.03	9.97		7.45
2.00	9.83	9.03		6.15
2.50		8.01		
3.00	7.16	6.81		3.73

TABLE 4

Values of the "salting-out" constant

SALT	"SALTING OUT" CONSTANT β	SOURCE
LiCl	0.192	Larsson (8)
NaCl	0.177	Larsson (7)
KCl	0.138	Chase and Kilpatrick (2)
$LiNO_3$	0.078	Larsson (8), Haessler (3) and Kolthoff and Bosch (6)
$NaNO_3$	0.080	Larsson (8)
KNO_3	0.040	Larsson (8)
$NaClO_4$	0.062	Kolthoff and Bosch (6)

A comparison of the values of the dissociation constant of benzoic acid in potassium chloride solutions as determined by the kinetic method with those determined by means of the quinhydrone electrode shows that the results are not in agreement at concentrations above 2 molar. Repeated determinations by the two methods in 3 molar potassium chloride solution consistently show this discrepancy. With 3 molar sodium chloride a

TABLE 5

The mean activity coefficient of the ions of benzoic acid at 25°C.

ELECTROLYTE CONCENTRATION SALT + NaB	$\sqrt{f_H f_B}$			
	LiCl	NaCl	KCl	$NaClO_4$
moles per liter				
0.10	0.78	0.79	0.80	0.78
0.20	0.77	0.77	0.77	0.77
0.30			0.78	
0.40	0.76	0.80		0.80
0.50			0.80	
0.60	0.80	0.82		0.82
0.80	0.83	0.85	0.85	0.86
1.00	0.87	0.91	0.89	0.90
1.50	1.00	1.08	1.03	1.03
2.00	1.18	1.28	1.21	1.17
2.41	1.38			
2.50		1.60	1.41	
3.00	1.76	2.10	1.80	1.61

TABLE 6

The mean activity coefficient of the ions of benzoic acid at 25°C.

ELECTROLYTE CONCENTRATION SALT + NaB	$\sqrt{f_H f_B}$				
	$LiNO_3$	$NaNO_3$	KNO_3	$C_6H_5SO_3Na$	p-$C_6H_4(CH_3)SO_3Na$
moles per liter					
0.10	0.79	0.79	0.78	0.78	0.78
0.20	0.76	0.76	0.76	0.74	0.74
0.25				0.73	
0.40	0.74	0.76	0.75	0.72	0.71
0.50				0.72	
0.60	0.76	0.77	0.76		0.71
0.80	0.77	0.80	0.78	0.71	0.71
1.00	0.79	0.82	0.80	0.72	0.71
1.20			0.82		
1.25				0.74	
1.50	0.87	0.91		0.79	
2.00	0.95	1.00			
2.50		1.13			
3.00	1.23	1.26			

similar discrepancy exists. In order to investigate this difference the assumptions of the kinetic method were tested further. The assumptions involved in the determination of $k_{H_3O^+}$ are as follows: (1) The hydrogen ion is the sole catalyst. (2) The energy of activation is constant within the experimental error of measurement from 0° to 35°C. (3) The energy of activation is independent of the salt concentration.

TABLE 7

The temperature coefficient in benzoate buffers

SALT	SALT + NaB	k_{35}/k_{25}	DEVIATION FROM 3.455
	moles per liter		
NaB	0.005	3.469	0.011
KCl	0.10	3.384	0.071
	0.50	3.505	0.050
	1.00	3.474	0.019
	1.50	3.457	0.002
	2.00	3.395	0.060
	3.00	3.519	0.064
NaCl	2.00	3.417	0.038
	3.00	3.168*	
	3.00	3.113*	
	3.00	3.148*	
$NaClO_4$	3.00	3.504	0.049
LiCl	3.00	3.379	0.076
$NaNO_3$	3.00	3.443	0.012
$C_6H_5SO_3Na$	1.00	3.423	0.032
p-$C_6H_4(CH_3)SO_3Na$	1.00	3.546	0.091
Average		3.455	±0.044

* Omitted from the average.

TABLE 8

The effect of reaction products upon the velocity constant

HB	KCl + NaB	k OBSERVED	$C_{H_3O^+} \times 10^4$	$K_c \times 10^5$
moles per liter	*moles per liter*			
0.005	3.00	0.01580	0.2590	5.22
0.005	3.00	0.01523	0.2497	5.03
0.005	3.00	0.01488	0.2440	4.91

To test these assumptions the dissociation constant of acetic acid in potassium chloride solutions was determined electrometrically. At the same time independent kinetic determinations were made on the same buffer solutions. Both methods gave results in agreement over the range from 0.10 to 3.0 molar potassium chloride concentration (5). Similar agreement was found for glycolic acid–glycolate buffers in potassium chloride solutions. Evidently the discrepancies at 3 molar salt concentration in the case of benzoic acid are not due to the invalidity of the assumptions. In fact, the results indicate that the high primary salt effect is not connected with any catalytic effect of the hydrochloric acid molecules. Any explanation of the difference in the results must therefore be related to the benzoic acid buffer itself or to some specific reaction with the acetal, or to the products of the reaction. Varying the buffer ratio has little effect on the calculated dissociation constant. It is not possible to vary the acetal

TABLE 9

Comparison with equation 5

ELECTROLYTE MOLES PER LITER	$\sqrt{f_H f_B}$ OBSERVED	$\sqrt{f_H f_B}$ CALCULATED	ELECTROLYTE MOLES PER LITER	$\sqrt{f_H f_B}$ OBSERVED	$\sqrt{f_H f_B}$ CALCULATED
$NaClO_4$ (B = −0.222)			KNO_3 (B = −0.176)		
0.10	0.78	0.80	0.10	0.78	0.79
0.20	0.77	0.78	0.20	0.76	0.76
0.40	0.80	0.79	0.40	0.75	0.75
0.60	0.82	0.82	0.60	0.76	0.77
$NaCl$ (B = −0.218)			$LiNO_3$ (B = −0.166)		
0.10	0.79	0.80	0.10	0.79	0.79
0.20	0.77	0.77	0.20	0.76	0.76
0.40	0.80	0.78	0.40	0.74	0.75
0.60	0.82	0.82	0.60	0.76	0.76
KCl (B = −0.216)			$C_6H_5SO_3Na$ (B = −0.124)		
0.10	0.80	0.80	0.10	0.78	0.78
0.20	0.77	0.77	0.20	0.74	0.74
0.30	0.78	0.77	0.25	0.73	0.73
0.50	0.80	0.80	0.50	0.72	0.72
$LiCl$ (B = −0.192)			p-$C_6H_4(CH_3)SO_3Na$ (B = −0.114)		
0.10	0.78	0.79	0.10	0.78	0.78
0.20	0.77	0.77	0.20	0.74	0.74
0.40	0.76	0.76	0.40	0.71	0.71
0.60	0.80	0.79	0.60	0.71	0.71
$NaNO_3$ (B = −0.178)					
0.10	0.79	0.79			
0.20	0.76	0.76			
0.40	0.76	0.75			
0.60	0.77	0.77			

concentration very greatly, but the effect of the products of hydrolysis was tested in the following manner. An experiment was carried out in the usual way; the buffer solution was then drawn back into the mixing chamber, another portion of acetal was added, and the experiment repeated. Upon completion of this experiment the process was repeated. The results are given in successive order in table 8. Although there is about 6 per cent change in the $k_{\text{obsd.}}$ and in the resultant dissociation constant, the magnitude of this effect cannot account for the 20 per cent difference between the results by the two methods in 3 molar potassium chloride solution. In no case did the velocity constants show a trend.

As pointed out by Chase and Kilpatrick (2) the mean activity coefficient of the ions of benzoic acid can be represented by an equation of the form

$$- \log \sqrt{f_H f_B} = \frac{0.5\sqrt{C}}{1 + \kappa b} + \beta C \tag{4}$$

where κ equals $0.33 \times 10^8 \sqrt{C}$ and b is the apparent average ionic diameter. The β is an empirical constant which should include salting-out and interaction effects. If we arbitrarily set b equal to 3.0×10^{-8} cm. the above equation becomes:

$$- \log \sqrt{f_H f_B} = \frac{0.5\sqrt{C}}{1 + \sqrt{C}} + BC \tag{5}$$

By plotting $\log \sqrt{f_H f_B} + \frac{0.5\sqrt{C}}{1+\sqrt{C}}$ against the concentration, B has been evaluated for each solvent salt. The observed and the calculated values up to 0.6 molar are given in table 9.

Over this range the order of decreasing activity coefficients is Na > K > Li. For the sodium salts one finds $ClO_4 > Cl > NO_3 > RSO_3$, but at higher concentrations the mean activity coefficients become greater in sodium chloride than in sodium perchlorate.

SUMMARY

1. The classical dissociation constant of benzoic acid has been determined kinetically in solutions of lithium chloride, sodium chloride, potassium chloride, lithium nitrate, sodium nitrate, potassium nitrate, sodium perchlorate, sodium benzenesulfonate, and sodium *p*-toluenesulfonate.

2. From the values of the activity coefficient of molecular benzoic acid and the thermodynamic dissociation constant, the mean activity coefficients of the ions of benzoic acid in the several salt solutions have been calculated.

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A STUDY OF THE BENZOIN REACTION. II

Negative Catalysis in the Benzoin Reaction

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INTRODUCTION

Having definitely established the fact that pure potassium cyanide and benzaldehyde in the absence of water do yield benzoin (2), attention was directed to the statement in the literature that water was necessary to induce the reaction. Preliminary experiments with various brands of potassium cyanide showed that certain commercial samples would not yield benzoin when shaken with pure benzaldehyde at 100°C. for 1 hour unless water were added. Further experiments showed that alkali halides and also hydrogen sulfide and sulfur can inhibit the benzoin reaction. The effect of increasing quantities of sodium and potassium chlorides (impurities likely to be present in commercial potassium cyanide), potassium iodide, and quinol on the benzoin reaction was examined (figures 1 and 2). The results show that these substances in sufficient quantity prevent the formation of benzoin in 1 hour, and that potassium iodide and quinol are particularly effective. The latter were tried because it is known that they are more effective than potassium and sodium chlorides in the inhibition of the oxidation of benzaldehyde.

TIME–YIELD CURVES IN PRESENCE OF INHIBITORS

Next, a series of experiments was made to obtain time–yield curves in the presence of various quantities of quinol, potassium iodide, and potassium chloride (figure 3). It will be seen that the curves thus obtained are of the same type as those yielded by pure potassium cyanide, with the difference, however, that a diminished quantity of potassium cyanide appears to be functioning in the heterogeneous reaction. (See figure 3, upper section, Curves IV and VI.) The homogeneous autocatalytic reaction is unaffected. Thus the curve obtained with 1 g. of potassium cyanide and 0.3 g. of quinol is almost identical, particularly in the earlier stage, with that given by 0.3 g. of pure potassium cyanide. In other words, 0.3 g. of quinol renders inactive 0.7 g. of potassium cyanide.

From the amount of benzoin obtained in 1 hour, we can determine how much cyanide is effective in producing it. This determination is facilitated

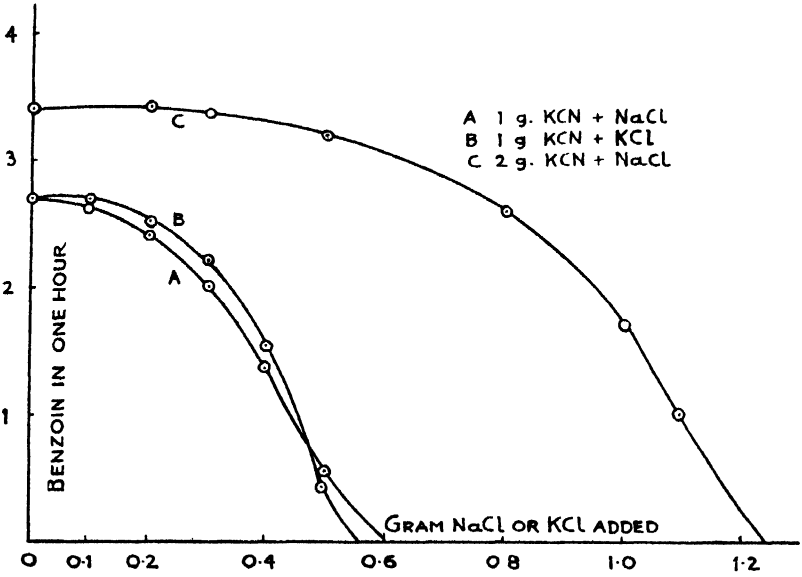

FIG. 1. EFFECT OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE ON THE YIELD OF BENZOIN

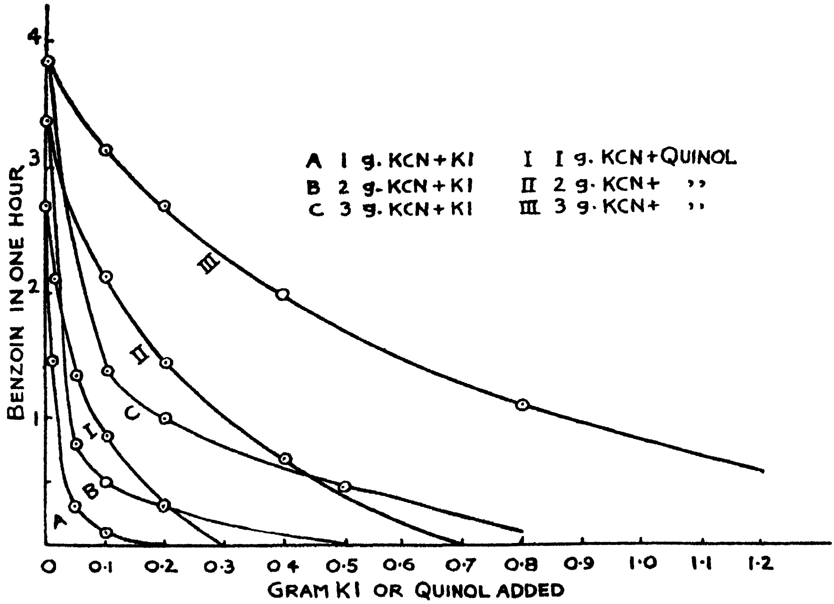

FIG. 2. EFFECT OF POTASSIUM IODIDE AND QUINOL ON THE YIELD OF BENZOIN

by plotting the quantity of benzoin obtained in 1 hour from 10 g. of benzaldehyde at 100°C., against the quantity of pure cyanide required to produce it, the correction of 0.17 g. (see Part I) being inserted. The yield of benzoin produced in 1 hour in any experiment with pure potassium cyanide and the added impurity is referred to this graph, from which the amount of

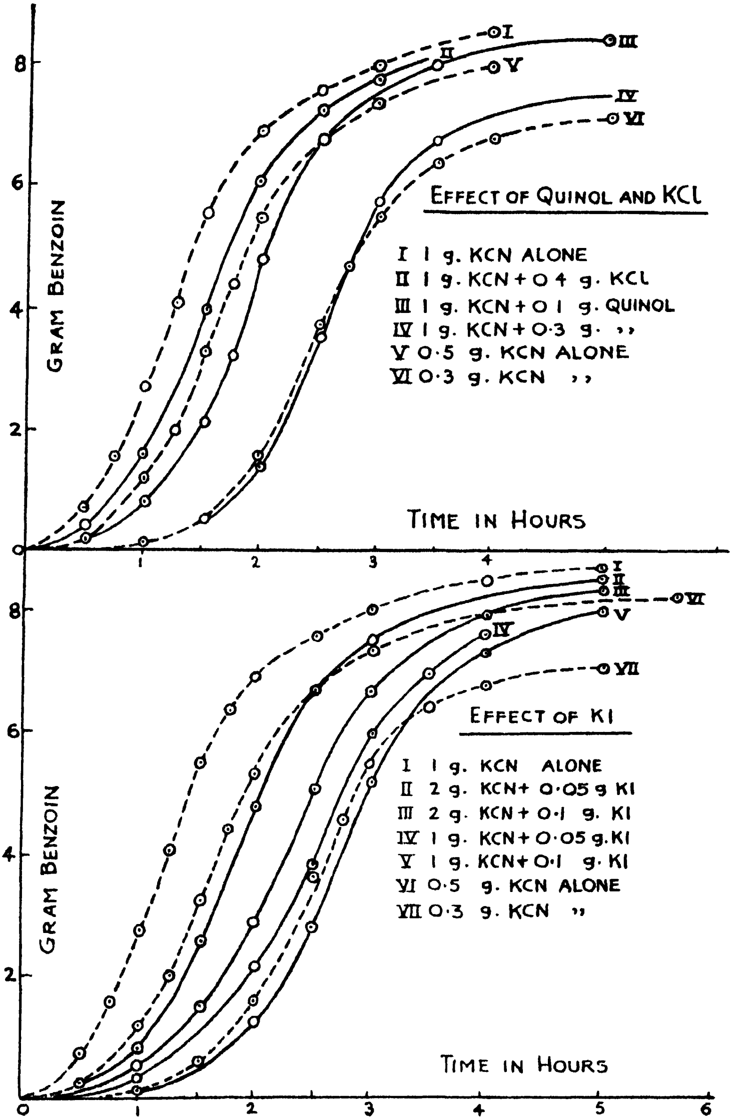

FIG. 3. EFFECT OF QUINOL AND POTASSIUM CHLORIDE ON THE YIELD OF BENZOIN; EFFECT OF POTASSIUM IODIDE ON THE YIELD OF BENZOIN

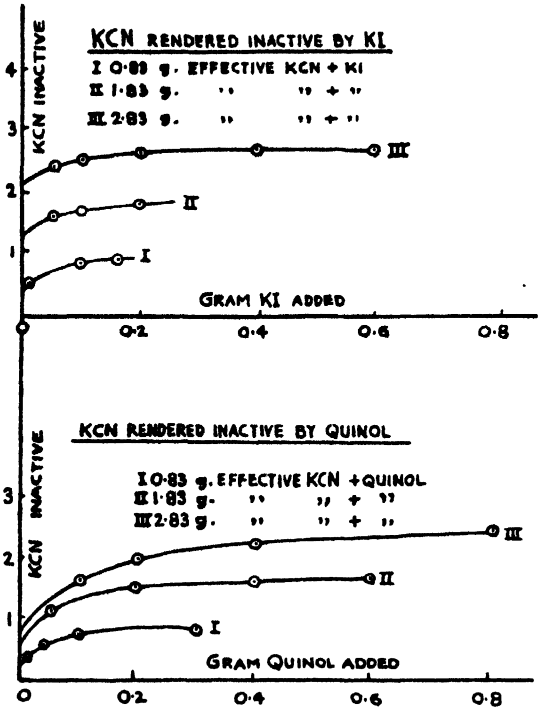

Fig. 4. Potassium Cyanide Rendered Inactive by Potassium Iodide and by Quinol

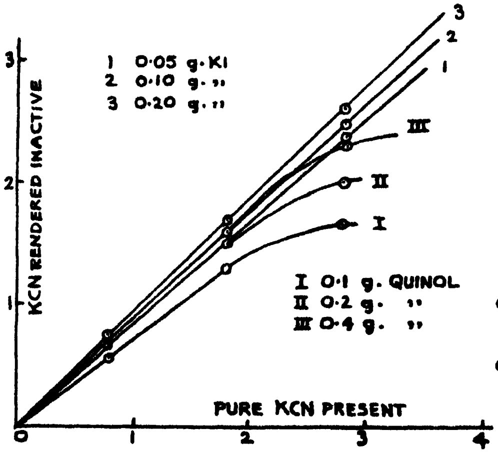

Fig. 5

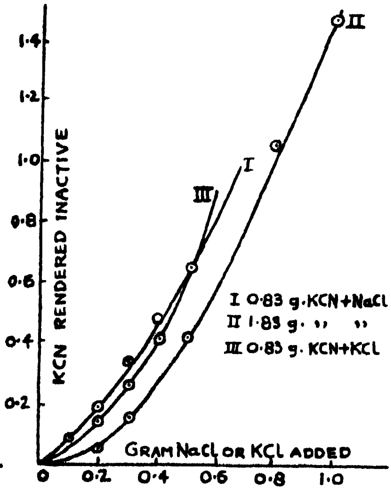

Fig. 6

Fig. 5. Potassium Cyanide Rendered Inactive by Potassium Iodide or Quinol, Plotted Against Pure Potassium Cyanide

Fig. 6. Potassium Cyanide Rendered Inactive by Sodium Chloride or Potassium Chloride

pure potassium cyanide required to produce the same yield of benzoin is found; the cyanide rendered inactive by the impurity added is obtained by subtraction.

THE DEACTIVATION OF POTASSIUM CYANIDE BY MEANS OF POTASSIUM IODIDE AND QUINOL

Figure 4 shows the quantities of potassium cyanide rendered inactive by various quantities of potassium iodide and quinol. With potassium iodide the quantity of cyanide rendered inactive increases very slowly with the potassium iodide added. Further, the amount rendered inactive by potassium iodide is proportional to the quantity of pure potassium cyanide present (figure 5, Curves 1, 2, 3).

These results can be interpreted to mean that potassium iodide is adsorbed on the surface of the solid potassium cyanide, and thus inhibits the reaction. The amount adsorbed is in equilibrium with the saturated solution of potassium iodide in benzaldehyde, and therefore is directly proportional to the amount of cyanide present. It is clear from the small quantities of potassium iodide required that little is adsorbed and little is required to saturate the benzaldehyde; about 90 per cent of the cyanide is rendered inactive by the potassium iodide.

Quinol behaves in much the same way as potassium iodide. Increase in the amount of quinol increases the inhibiting effect rapidly at first, and then more slowly. The quantities of quinol required to deactivate the potassium cyanide are larger than with potassium iodide.

It will be seen (figure 5) that up to a limit the quantity of potassium cyanide rendered inactive by a given quantity of quinol is proportional to the amount of potassium cyanide present.

DEACTIVATION OF POTASSIUM CYANIDE BY MEANS OF POTASSIUM AND SODIUM CHLORIDES

Potassium and sodium chlorides (figure 6) are less effective than potassium iodide and quinol and give results of a different type. The inhibiting effect increases with the quantity added. This may mean direct action between solid cyanide and solid chloride. The extent of the surface of the potassium cyanide rendered inactive will then increase with the quantity of the negative catalyst present, since it is more likely to be in contact with it. Presumably potassium and sodium chlorides are much less soluble in benzaldehyde than is potassium iodide.

DISCREPANCIES IN PREVIOUS RESULTS

These results explain the discrepancies in the results of previous workers, regarding the possibility of obtaining benzoin from benzaldehyde and potassium cyanide only. Where it was not obtained, impure cyanide had evidently been used. Lachmann's result (1) that benzoin can replace water in promoting the benzoin reaction can be referred to the fact that in the presence of benzoin the homogeneous autocatalytic reaction which is not affected by the inhibitor can proceed. The action of water in the presence of inhibitors is considered in Part III.

SUMMARY

1. It is shown that potassium and sodium chlorides, potassium iodide and quinol can inhibit the benzoin reaction.

2. They act by stopping the heterogeneous reaction, but they do not affect the homogeneous autocatalytic reaction.

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A STUDY OF THE BENZOIN REACTION. III

The Effect of Water on the Benzoin Reaction

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Having studied the reaction between potassium cyanide and benzaldehyde under anhydrous conditions (Parts I and II), it is of interest in view of the importance hitherto attributed to the cyano ion in the reaction to examine the effect of addition of water. Figure 1 gives the results of experiments at 100°C. with 10 g. of benzaldehyde and various quantities of potassium cyanide and water. No benzoin was obtained from 0.175 g. of potassium cyanide and 2.0 g. or more of water, nor from 0.17 g. of potassium cyanide even with as little as 0.1 g. of water.

It is clear from the curves that addition of water to a given quantity of potassium cyanide first increases and then reduces the rate of reaction. Autocatalysis gradually disappears. While this persists the curves obtained are similar to those yielded by suitable quantities of potassium cyanide in the absence of water (see figure 2).

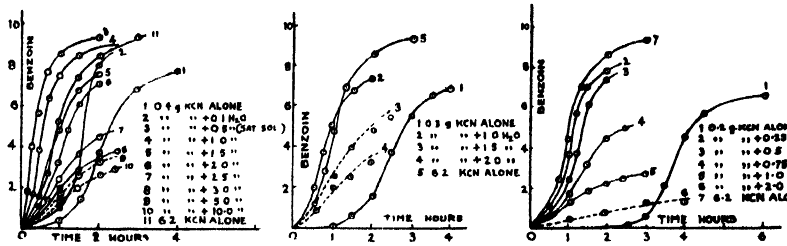


FIG. 1.

The dotted lines represent calculated curves, with experimental points thereon

Table 1 gives the quantities of solid anhydrous potassium cyanide which correspond to certain strong solutions as regards the rate of production of benzoin in the heterogeneous reaction (see Part I, p. 733). The accelerating and subsequent decelerating effect of water is well brought out. Figure 3 shows that solutions of different strengths in suitable quantities can give similar results.

It is evident that with concentrated solutions of cyanide there are again two reactions involved. From the similarity of the curves obtained with anhydrous potassium cyanide and with strong solutions, the homogeneous autocatalytic reaction appears under these circumstances to be unaffected by the presence of water. The heterogeneous reaction between the strong solution and benzaldehyde is greatly accelerated.

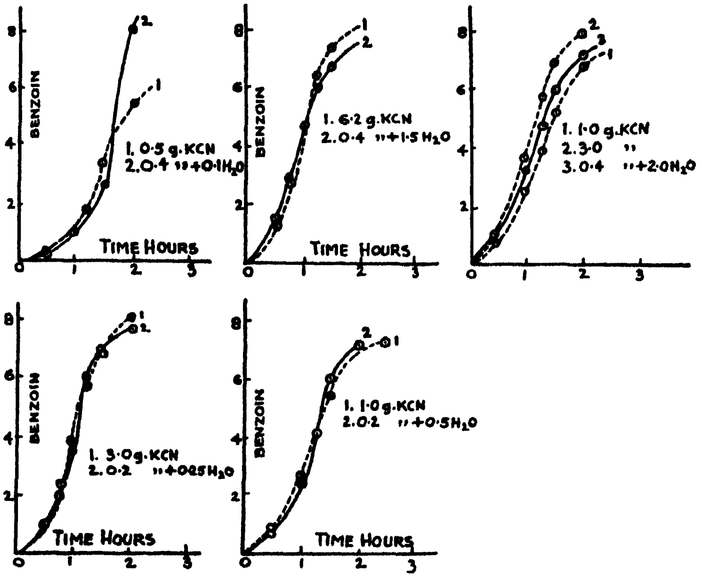


FIG. 2.

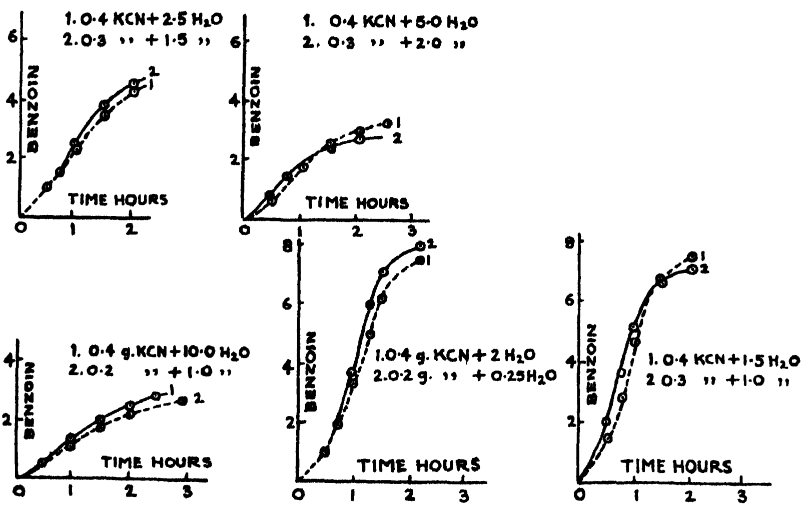


FIG. 3.

The rapid fall in the rate of reaction with the addition of water beyond a certain limit may be referred to the fact that as the cyanide solution decreases in strength it extracts in increasing proportion the trace of cyanide dissolved in benzaldehyde which is producing the homogeneous reaction.

It is of interest to attempt to formulate mathematically the reaction occurring between the aqueous solution and benzaldehyde when sufficient water is present to stop the homogeneous reaction.

We may proceed as follows:

Let A = number of grams of benzaldehyde originally present.
y = number of grams of benzaldehyde present at time t.
$\frac{A-y}{2}$ = relative number of molecules of benzoin present.
$\frac{A+y}{2}$ = total number of molecules present.

TABLE 1

Quantities of solid anhydrous potassium cyanide corresponding to certain strong solutions

KCN TAKEN A	H_2O ADDED	EFFECTIVE KCN $(A - 0.17)$	YIELD OF BENZOIN IN ONE HOUR	EQUIVALENT EFFECTIVE ANHYDROUS KCN
grams	*grams*	*grams*	*grams*	*grams*
0.2	0.0	0.03	Nil	0.03
0.2	0.25	0.03	3.6	2.22
0.2	0.50	0.03	2.4	0.64
0.3	0.0	0.13	0.12	0.13
0.3	1.0	0.13	5.0	6.5
0.4	0.0	0.23	0.3	0.23
0.4	0.1	0.23	0.9	0.31
0.4	1.5	0.23	4.7	5.45
0.4	2.0	0.23	3.2	1.43

We assume that the rate of reaction is proportional to a constant depending upon the cyanide and water present and on the molecular concentration of benzaldehyde. The reason for this is that by a process of trial and error, it has been found that this assumption gives better results than that involving the square of the benzaldehyde concentration. We have therefore for a solution,

$$-\frac{dy}{dt} = k\,\frac{y}{\frac{A+y}{2}}$$

$$= \frac{2ky}{A+y}$$

and

$$-2k(t+c) = y + A \ln y$$

Therefore

$$t + c = \frac{y + 23.0 \log y}{-2k}$$

When $t = 0$, $y = 10$, so,

$$c = \frac{33}{-2k} = \frac{-16.5}{k}$$

$$-2k = 2\,\frac{16.5}{c} = \frac{33}{c}$$

Therefore,

$$t + c = \frac{c(y + 23.0 \log y)}{33}$$

TABLE 2

Values of k for various solutions

KCN TAKEN	EFFECTIVE KCN	WATER ADDED	c	$k = \frac{-16\ 5}{c}$
grams	*grams*	*grams*		
0 175	0 005	1 0	−34	0.49
0 2	0 03	2 0	−46	0 36
0 2	0 03	1 0	−12.3	1 34
0 2	0 03	0 75	−8 0	2 1
0 3	0 13	2 0	−8 8	1 9
0 3	0 13	1 5	−5 8	2 8
0 4	0 23	10 0	−13	1 3
0 4	0 23	5 0	−8 8	1 9
0.4	0 23	3.0	−7 2	2 3
0 4	0 23	2 5	−6 3	2 6

In figure 1 the curves indicated by dotted lines have been calculated by means of the above equation, with suitable values for *c*. While the agreement is not exact, the equations reproduce the general course of the experimental curves.

Table 2 gives the values of *k* for various solutions considered. In figure 4 these values are plotted against the quantities of water used. The curves for the same quantity of cyanide are regular.

THE EFFECT OF INHIBITORS IN THE PRESENCE OF WATER

It was shown by Lachmann (1) that potassium cyanide which did not yield benzoin with benzaldehyde alone, reacted when water was added. Water has thus the power of decreasing the inhibiting effect of the negative catalysts present in the cyanide. With a view to studying the effect of negative catalysts in the presence of water some experiments were carried out on the addition of potassium iodide to solutions of pure potassium cyanide in water (figure 5). It will be seen that 0.1 g. and 0.2 g. of potassium iodide with 0.2 g. of potassium cyanide and 0.25 g. of water do reduce the rate of reaction, but the effect is more marked in the absence of water; 0.1 g. of potassium iodide will prevent completely 0.2 g. of anhydrous potassium cyanide from reacting.

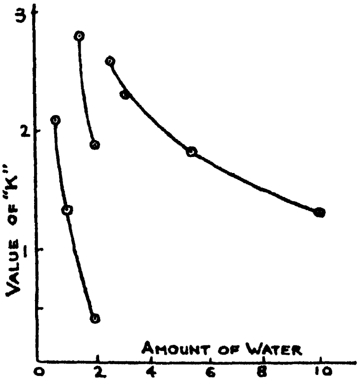


FIG. 4.

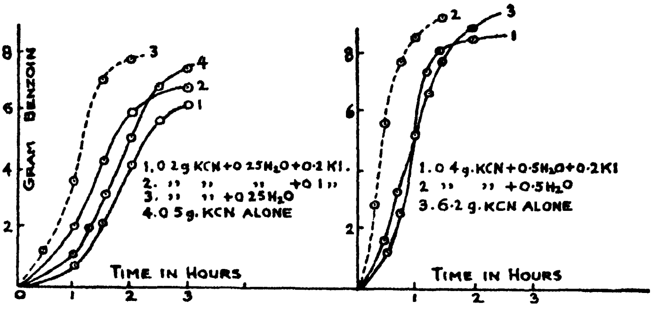


FIG. 5.

TABLE 3

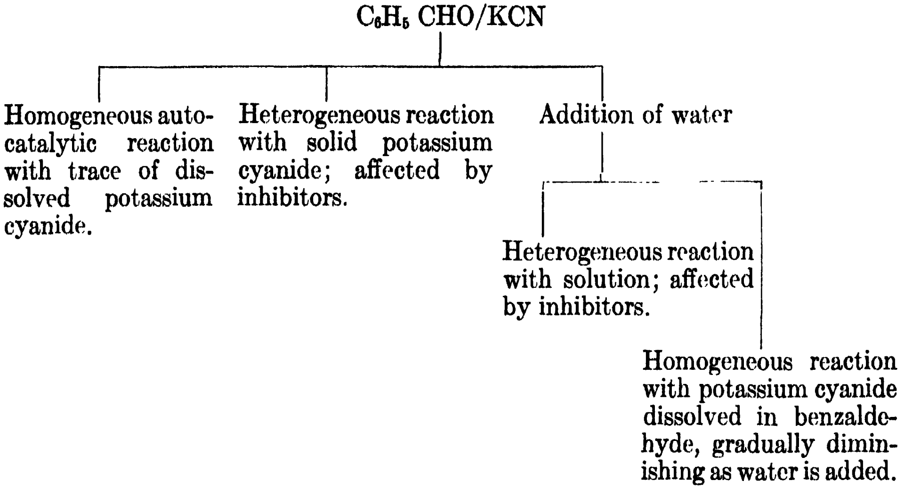
The equivalents in terms of anhydrous potassium cyanide of the solution containing potassium iodide

KCN TAKEN	WATER ADDED	IMPURITY ADDED	EFFECTIVE KCN $A - 0\ 17$	BENZOIN IN ONE HOUR	EQUIVALENT EFFECTIVE ANHYDROUS KCN
grams	*grams*		*grams*	*grams*	*grams*
0 2	0 25	Nil	0 03	3 6	2 22
0.2	0 25	0 1 KI	0 03	2 01	0 48
0 2	0 25	0 2 KI	0.03	0 72	0 23
0.4	0 5	0 2 KI	0 23	5 2	7 1

Figure 5 also compares the results with curves obtained in the absence of water. It will be seen that the curves with potassium iodide in the presence of strong solutions of potassium cyanide are of the same type as those obtained with anhydrous potassium cyanide, so that we can deduce the equivalents in terms of anhydrous potassium cyanide of the solution containing potassium iodide (see table 3).

Lachmann's result quoted above was thus due to the capacity of water to reduce the effect of the negative catalysts.

The results obtained in the investigations described in Parts I, II, and III of this study of the benzoin reaction may be summarized as follows:


C_6H_5 CHO/KCN
Homogeneous autocatalytic reaction with trace of dissolved potassium cyanide.
Heterogeneous reaction with solid potassium cyanide; affected by inhibitors.
Addition of water
Heterogeneous reaction with solution; affected by inhibitors.
Homogeneous reaction with potassium cyanide dissolved in benzaldehyde, gradually diminishing as water is added.

REFERENCE

(1) Lachmann: J. Am. Chem. Soc. **46**, 708 (1924).

COMMUNICATION TO THE EDITOR

ON THE $(C—C)_{diam}$ BOND ENERGY

The most probable experimental value for the heat of sublimation of carbon is 154 ± 10 Cal. W. E. Vaughan and G. B. Kistiakowsky (Phys. Rev. **40,** 457 (1932)) calculate 161 to 176 Cal., with the assumption of a considerable amount of C_2 in equilibrium in the saturated carbon vapor.

Theoretically, the heat of sublimation S_C corresponding to the process

$$C(^5S)_{diam} \rightarrow C(^3P)_{gas} - S_C$$

is given by

$$S_C = 2E_{CC} - E^* \tag{1}$$

where E_{CC} is the energy of the $[C(^5S) - C(^5S)]_{diam}$ bond and E^* the energy difference between the ^5S and ^3P states of carbon (according to the Heitler-London valency theory, C_{diam} is in the ^5S state).

Recently R. F. Bacher and S. Goudsmit (Phys. Rev. **46,** 948 (1934)) have found from B. Edlén's measurements (Z. Physik **84,** 746 (1933)) the value $E^* \sim 4$ v.e. = 92 Cal., instead of the former value $E^* \sim 1.6$ v.e. = 37 Cal. (Heitler, W., and Herzberg, G.: Z. Physik **53,** 52 (1929)).

Equation 1 must therefore be written

$$154 \pm 10 \text{ Cal.} = 2E_{CC} - 92 \text{ Cal.}$$

Consequently

$$E_{CC} = 123 \pm 5 \text{ Cal.}$$

and not 70 to 80 Cal. as is generally accepted.

The usual value $E_{CC} \sim 75$ Cal. would give, according to equation 1, $S_C \sim 60$ Cal., which is very improbable since, for example, the heat of sublimation of copper is 70 Cal.

A cycle starting from C_2N_2 ($\frac{1}{2}$ $C_2N_2 \rightarrow CN - 38$ Cal. (Kistiakowsky, G. B., and Gershinowitz, H.: J. Chem. Physics **1,** 432 (1933); Mooney, R. B., and Reid, H. G.: Proc. Roy. Soc. Edinburgh **52,** 152 (1932)), with the new value of E^* and with the exact value of $D_{N_2} = 169.47 \pm 0.11$ Cal. recently obtained by G. Buttenbender and G. Herzberg (Ann. Physik **21,** 577 (1935)) ($D_{N_2} \sim 208$ Cal. was the value used formerly for thermochemical calculations), gives for the dissociation energy of CN:

$$CN(X^2\Sigma) \quad C(^3P) + N(^4S) - 165 \pm 3 \text{ Cal. } [7.2 \text{ v.e.}] \tag{2}$$

or

$$CN(X^2\Sigma) \rightarrow C(^5S) + N(^4S) - 257 \pm 3 \text{ Cal.} \tag{3}$$

The value $D_{CN} = 7.2$ v.e. corresponding to equation 2, which gives a carbon atom in the ^3P state, is in good agreement with $D_{CN} = 7.09$ v.e. obtained by R. S. Mulliken (Rev. Modern Physics **4,** 1 (1932)) from spectroscopical data on the lower $X^2\Sigma$ state of CN.

It is clear that the new values of E^*, D_{N_2}, and especially E_{CC} lead to important consequences for many problems of molecular structure and chemical calculations (cf. Norrish, R. G. W.: Free Radicals. General Discussion of the Faraday Society September, 1933, p. 103).

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March 28, 1935.

NEW BOOKS

Neuere massanalytische Methoden. By E. **Brennecke**, K. **Fajans**, N. H. **Furman**, and R. **Lang**. 25 x 16 cm.; xi + 211 pp., with 15 diagrams. Stuttgart: Ferdinand Enke, 1935. Price: unbound, 18.00 RM; bound, 19.80 RM.

This work is divided into six sections: Section I, dealing principally with a standardized method of determining indicator corrections in acid-alkali titrations; Section II, giving full details of the use of ceric sulfate in volumetric analysis; Section III, describing titrations by means of standard iodate or bromate solutions, as developed chiefly by Andrews, Lang, Berg and Manchot and Oberhauser; Section IV, setting out the advantages of chromous salts as standard reducing agents, and giving full details of the necessary indicator electrode and of many useful applications; Section V, a discussion of the principles and uses of oxidation-reduction indicators; Section VI, an account of the theory and practice of the use of adsorption indicators.

The names of the collaborators are a sufficient guarantee that the treatment of the sections associated with their work is authoritative; and in the last section, particularly, much useful and, in some cases, hitherto unpublished information is discussed in a concise and clear manner.

The references testify to a careful search of the literature. The inclusion of an author from the U. S. A. may be partly responsible for an impartial treatment of the literature from that country, but British chemists, too, receive justice in this respect, although some of them suffer from incorrectly spelt names and one of them is given a wrong initial. Apart from this there are very few typographical errors.

The work can confidently be recommended as being a comprehensive and careful survey of the vast mass of recent material which falls within its purview. Its price, however, as with so many new German books, is high even in terms of currencies on a gold standard, and is almost prohibitive in terms of depreciated pounds and dollars. This is unfortunate, for the book merits a wide circulation, particularly because it shows that there is a fruitful field in which analysts and physical chemists can coöperate with mutual advantage.

A. D. Mitchell.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 17 cm. Berlin: Verlag Chemie, 1934. (1) System Nummer 35: Aluminium. Teil B, Lieferung 2; pp. xvi + 309—13. Price: 49 RM. (2) System Nummer 4: Stickstoff. Lieferung 1; pp. v + 292. Price: 43 RM. Subscription price: 38 RM.

(1) The section on aluminium deals with the silicates and double silicates, and contains a long and interesting section on ultramarine, in which the recent literature is very fully covered. The alums and the aluminates are also included. The text is fully illustrated by phase rule diagrams and the results of physical and physicochemical methods are considered in detail. This section of the work is of special interest from the point of view of physical chemistry and constitutes an invaluable source of information on many subjects of considerable technical interest.

(2) The volume on nitrogen deals with the general chemistry of the element, including natural ammonia fixation and nitrification, with the physical and physico-

chemical properties of nitrogen (a very full account of the spectra being included), and with active nitrogen. The account of the technical production of nitrogen includes patent literature. There is a good discussion of the atomic weight of nitrogen in which analyses of a large number of researches are set out in a very clear and instructive form. This first section of the volumes on nitrogen is very complete and of high standard, and covers a very extensive field of literature.

J. R. PARTINGTON.

Free Radicals. A general discussion held by the Faraday Society. 25 x 15.5 cm.; 2 + 248 pp. London: Gurney and Jackson, 1934. Price: bound, limp cloth, 12/6.

Once more the Faraday Society has placed physical chemists under a debt of gratitude. The reports of the discussions which they organize at frequent intervals are now well-known and highly appreciated, alike by those who are, and those who would be, up-to-date in their knowledge of the latest developments. By bringing together distinguished workers in a special field, hearing and answering questions, they not merely present the subject but present it alive.

This volume is most timely and will be most welcome. It indicates how much preparatory work has already been achieved—work on the existence and preparation of free radicals—and these results are discussed by the men who have attained them. It also shows how the application of exact physiochemical methods to the available material may now be expected to lead to important conclusions.

The first part (12 papers) deals with free radicals of relatively long life; the second with those of short life, and this is subdivided into chemical aspects (A) general and inorganic (5 papers), B, hydrocarbons (7 papers). The third part deals with the physical aspects of radicals of short life (5 papers).

Part I opens with an account of prevalent carbon radicals, followed by a short paper by Schönberg on a new class of radicals having a free sulfur bond. Sugden gives an account of magnetism in free radicals due to an odd number of electrons. Sulfur monoxide and oxygen are discussed; theoretical papers are contributed by Hückel, Lennard Jones, and Ingold; electronic levels are dealt with by Snow and Allsopp and the C=C double bond is specially considered.

Part II opens with an account by Norrish of the photochemical production of free radicals, followed by a theoretical paper by Franck and Rabinowitsch. Part II B contains important contributions by Bone, Rice, Paneth, Hartel, Polanyi, and others.

Part III has an introductory paper by Mecke on free radicals and spectroscopy, and an account of the positive ray method of investigating the decomposition of hexane by Conrad (with some excellent photographs). There are papers by Harkins and by Willey on free radicals produced in the electric discharge, and one by Semenoff on the transference of energy in collisions.

Taken together, the papers and discussions give an admirable idea of the state of knowledge and opinion on a subject which has only recently begun to attract much attention; they are very suggestive of developments in the near future. Much light is being thrown on the problems of molecular stability and molecular change.

E. B. LUDLAM.

Gasentladungstabellen. Tabellen, Formeln und Kurven zur Physik und Technik der Elektronen und Ionen. By M. KNOLL, F. OLLENDORFF, AND R. ROMPE (with the collaboration of A. Roggendorf). 25 x 17 cm.; x + 171 pp. Berlin: Springer, 1935. Price: 29RM (in cloth).

The authors have attempted to give in this volume, in as convenient a form as possible, all the data likely to be required by workers with the discharge of ions and electrons through gases at moderate down to very low pressures. These are by no means the least coy or elusive of the more out-of-the-way data of physics, and their tracing down, even in relatively simple special cases, taxes or overtaxes the resources even of a large library. In many sections of the subject, sufficiently precise and extended numerical data were practically nonexistent a few years ago, and all workers—even those favored ones who have enjoyed the help of a more experienced hand in the same laboratory—must have felt acutely the need for tables of the kind now under review.

The book therefore undoubtedly fills a serious gap in the literature. The completeness of the filling can only properly be judged after prolonged use of the book in the laboratory. The less stringent test of a fairly close inspection reveals no serious omissions or errors in the work, which contains not only a comprehensive summary of the relevant properties of atoms, molecules, electrons, ions, and photons, but also the equivalent of "workshop hints" on the materials in common use in discharge tubes, and on high vacuum technique, together with a useful collection of mathematical formulæ and tables.

Some minor criticisms may be offered, mainly on matters of form; for instance, the unjustifiable piling up of *un*significant figures on some of the data, and the habit of referring the more inquisitive reader to the *Handbuch der Physik* or similar works, and not to the original papers These points do not however affect the general utility of the book.

The price is somewhat high, especially in sterling, but the book, with its elaborate tables and large number of specially drawn curves, cannot have been a cheap one to produce.

H. R. ROBINSON.

Rontgenoskopie und Elektronoskopie von dispersen Systemen, Faden, Filmen, und Grenzschichten. Sonderheft der Kolloid-Zeitschrift, Bd. 69, H. 3. Edited by Wo. Ostwald (12 contributors). 27 x 19.5 cm.; 138 pp. Dresden and Leipzig: Steinkopff, 1935. Price: 9 RM (stiff paper cover).

This volume presents the contributions of Ostwald, Schiebold, Brill, Fricke, Halle, Astbury, Hofmann, Saupe, Wever, Rupp, Trillat, and Bruche to the General Meeting of the Kolloid-Gesellschaft in Hanover in September, 1934. It provides a useful and authoritative general sketch for those wishing to acquire some familiarity with these comparatively new applications of x-ray and electron optics, with some hundreds of references to original papers which will be invaluable to those whose interests are more specialized.

H. R. ROBINSON.

Dizionario di Chimica generale e industriale. Volume II. F–Z. By MICHELE GIUA AND CLARA GIUA LOLLINI. 29 x 20 cm.; iii, 71 + 1137 pp. Turin: Unione Tipografico-Editrice Torinese, 1934. Price: 175 lire.

This second, and final, volume of the Dictionary of Chemistry, containing 54 more pages of text than the first volume, covers the headings F–Z. Thus it is evident that, even when allowance has been made for the difference in the Italian alphabet, the matter in this volume has been more condensed than in the previous one. The second volume contains 23 full page plates and 521 illustrations in the text, as against 28, and 565, respectively, in the first. In addition, the second volume includes 71 pages of comprehensive index to the whole, 2 pages of corrections, and a list of journals with their quoted abbreviated titles.

The dictionary is comprehensive, dealing not only with pure chemistry, but also its application and connection with agriculture, biology, medicine, geology, etc.; it includes also biography. The biographies number altogether some 722 (living chemists have not been included); in many cases these are very brief, e.g., only 4 lines are devoted to Volta and rather more to Faraday, although fairly full references are appended to each from which fuller information may be sought. Further, in the case of the former, more information is found in the text under such headings as galvanic pile, electrochemistry, methane, and eudiometry, the cross references to which are not quoted in the biography. Among the biographies one notices names like Marsh, Kipp, and Selmi, but the absence of others, e.g., Hooke, Mayow, Watson, Hales, Rayleigh, and LeChatelier.

A special feature has been made of phase rule diagrams, especially in the case of metals; this is to be expected as the authors had previously published a book on chemical combination among metals, which was translated into English by Robinson in 1918. Branches of chemistry especially important to Italy are detailed with much valuable information, e.g., vegetable and essential oils, mercury and its medicinal preparations, marbles etc.

The high standard of production of the previous volume has been fully maintained in the present one, and the whole constitutes a mine of interesting and accurate information.

W. H. PATTERSON.

Arsenical and Argentiferous Copper. By J. L. GREGG, with a foreword by H. Foster Bain. American Chemical Society Monograph. 189 pp. New York: The Chemical Catalog Co., Inc., 1934. Price: $4.00.

This monograph was prepared at the Battelle Memorial Institute under the sponsorship of the Calumet and Hecla Consolidated Copper Co. The author has made a thorough survey of the existing literature on the properties of arsenic- and silver-bearing copper and copper alloys, and in this monograph gives a detailed and critical discussion of the literature. He has not been satisfied with simply quoting the literature; he discusses it at length and attempts to explain the discrepancies and to bring out the correct facts and figures. In this he was considerably aided by use of hitherto unpublished data of research work done at Battelle and at the laboratories of the Calumet and Hecla company.

Not only has the author made an admirable review and summary of the literature, but he has added to it valuable new material. It is unfortunate that some of the curves have been reduced too much in printing, making it rather difficult to read them correctly. The reviewer is in agreement with the foreword that "The monograph constitutes one of the most authentic and complete, as it is certainly the most up-to-date, of compendiums on the properties and uses of the metals. Nowhere else will so much modern knowledge of this ancient metal be found in so few pages."

S. SKROWRONSKI.

Étude thermodynamique de la tension superficielle. By RAYMOND DEFAY. xi + 372 pp. Paris: Gauthier-Villars & Cie., 1934.

This book offers a detailed study of the thermodynamic treatment of capillary phenomena and of adsorption, applied not only to systems in equilibrium but also to irreversible transformations. Reaction velocity, catalysis, and velocity of adsorption are included in the topics treated by the author. The thermodynamic methods of Th. de Donder furnish a basis for much of the discussion.

This book can be commended to the attention of all serious students of the matters treated by the author.

F. H. MACDOUGALL.

The Aliphatic Free Radicals. By F. O. and K. K. RICE, with a foreword by F. A. Paneth. 204 pp. Baltimore: The Johns Hopkins Press, 1935. Price: $4.50.

Professor Rice and his wife have presented in this volume a problem for solution in the field of reaction mechanism which is of fundamental importance not only in the theoretical realm but also in many fields of industrial activity. That problem is the determination of the extent to which the path from an initial to a final state in a number of processes involving organic chemical molecules and their decompositions occurs through a series of steps involving the production of free radicals followed by a radical chain or chains. The authors show that, prior to Gomberg's isolation of free radicals in 1900, the quadrivalence of carbon was the practical basis of organic chemistry in the preceding period. It was, however, not the Gomberg work but the development of the photochemistry of atom reactions involving hydrogen, chlorine, bromine, etc., which in the interval from 1912 to 1925 laid the foundations for the examination of the rôle of organic radicals in reaction mechanism. Paneth and Hofeditz, in 1929, by demonstrating the existence of free methyl in the decomposition of metal methyls by heat at low pressures, carried the problem into the field of thermal reactions. Since 1929, the mental attitude of those interested has undergone a great change from frank derision, through scepticism to reluctant admission of the possibility of radical participation in organic mechanisms. Professor Rice and his associates are largely responsible for this change by their continued insistence on the supporting evidence and finally, with Herzfeld, by the demonstration that reactions kinetically simple as to reaction order can actually have a chain mechanism.

This book will be of great assistance in the research work which will be done in the next few years to provide a decisive answer, affirmative or negative, to the issue raised. It details methods of preparation and identification of free radicals, aliphatic in nature. It sets forth their properties, their lifetimes, their stabilities. A further chapter deals with bond energies and the effect of substitution and structure on bond strengths. It formulates the problem that must be solved,--that of the activation energies of reactions involving free radicals. At first sight such a problem may seem hopeless, but one can take courage from the progress that has been made with the corresponding atom reactions. There follow half a dozen chapters dealing with the various types of organic molecules that may give rise to free radicals by bond breakage, and a formulation and discussion in each case of hypothetical free radical mechanisms. A final chapter deals with the evidence for such mechanisms in organic liquid systems. The whole subject of radicals in reaction mechanism has been gathering momentum in recent years. Professor and Mrs. Rice have provided us with an excellent résumé of our knowledge as it now exists and a challenge to our judgment in these matters for the future.

HUGH S. TAYLOR.

Schwebstoffe in Gasen. Aerosole. By A. WINKEL and G. JANDER. 25 x 16 cm. 116 pp. Sammlung chemischer und chemisch-technischer Vorträge. Stuttgart: Ferdinand Enke, 1934. Price: 7.50 RM.

This monograph appears in the well known *Sammlung chemischer und chemisch-technischer Vorträge*, and deals with suspensions of fine particles of fog (mist or cloud), dust, and smoke in air or other gases. The subject is fairly well treated, both from a scientific and practical standpoint, and the book will be of value to colloid chemists, physicists, meteorologists, and military tacticians. The authors are familiar with the notable work of R. Whytlaw-Gray and his collaborators in this field, and devote a considerable amount of space to it. It is a pity, however, that they do not appear to know of the pioneer books of W. E. Gibbs (*Clouds and Smokes*, Churchill, London, 1924; and *The Dust Hazard in Industry*, Ernest Benn, London, (1925). These two books, together with the present one and the book by R. Whytlaw-Gray and H. S. Patterson (*Smoke, a Study of Aerial Disperse Systems*, Edward Arnold, London, 1932), give a comprehensive account of practically all aspects of the subject.

There is an interesting chapter in the present book on the electrical properties of aerosols—a subject of importance to aircraft pilots and meteorologists. The authors refer to the pioneer investigations of J. J. Thomson on the formation and stability of electrically charged droplets and of droplets whose surface tension is a function of the radius. These are both important subjects. It could not be expected that the authors would be familiar with that famous (or infamous) n-component system, the "London particular," i.e., the yellow smoky fog that used to occur so frequently in the winter months. This "meteoric" monster has now, however, practically vanished, owing to the increasing use of gas and electrical energy for heating and cooking, and of central heating systems employing oil or coke.

The reviewer can recommend the following simple lecture experiment on the electrical coagulation of an aerosol. Take an old-fashioned bell jar (one fitted with a tubulure and cork at the top). Stick a metal wire well through the cork, and connect it with the secondary of an induction coil. Lift the bell jar from its glass plate, burn a piece of magnesium wire under it, replace it on the plate, and start the coil. In a few seconds the magnesium oxide aerosol will come down as a beautiful "snow" storm (*verb. sap.*).

Although the specialist may detect certain *lacunae* in the book of Winkel and Jander, the authors have succeeded in compressing a great deal of highly interesting material into 111 pages, and their book may be recommended to a wide circle of readers.

F. G. Donnan.

From Galileo to Cosmic Rays. By Harvey Brace Lemon. 450 pp. Chicago: University of Chicago Press, 1934. Price: $5.00 (including stereoscope).

The title of this work might lead one to suppose it to be another popular treatment of certain aspects of modern physics addressed to the adult reading public. While the author states that he had the latter somewhat in mind, it is essentially a pandemic textbook of elementary physics designed for the undergraduates in the "Chicago System." The writer's statement in the preface that the need has been felt of such a text under one cover in preference to allowing the student to browse among selected passages from miscellaneous sources is interesting.

Since visual instruction is the watchword of the newer educational methods, the author has spared no trouble not only in illustrating the principles under discussion, but in providing marginal pen sketches on almost every page intended to enliven the subject and to catch and hold the reader's interest.

It is perhaps a matter for a psychologist to predict, or of experience to show, whether the desired end is to be attained in this way; whether, for example, comprehension of the principles of the components of force will be facilitated if accompanied by a sketch of a canal boat with all details including not only the mule and driver but the family laundry being dried en route; whether an Alaskan dog team, an Alpine climber, an East Indian student (or is it merely the proverbial wet towel) are all essential on one page to illustrate *work*. Will the imagination be stimulated by that which leaves nothing to the imagination? Or is the imagination which is so dull as to need stimulation worth the effort and expense?

The usual principles of physics are set forth, mainly following classical methods except in the matter of illustrations which undeniably are artistic and attractive. Although neutrons and positrons are described, one is surprised to find deuterium and deuterons neglected.

Those who are interested in a pandemic presentation of the principles of physics will find this work of undoubted value. It is not intended for a more serious or fundamental approach to the subject.

S. C. LIND.

The Science of Rubber. Handbuch der Kautschukwissenschaft. By K. MEMMLER, translated by R. F. Dunbrook and V. N. Morris. 770 pp. New York: Reinhold Publishing Corporation, 1934. Price: $15.00.

The editor has been assisted in the preparation of this treatise by seven collaborators, who join him in writing the various chapters into which the book is divided. The editors of the English edition have been assisted by a group of ten translators, all members of the Research Staff of the Firestone Rubber Company.

The author wisely chose to ignore plant practice in the fabrication of rubber products and the factory technology of rubber, so as to devote his efforts exclusively to the science of rubber production, treatment, and testing. In carrying out this object, he has given a thorough presentation of the botany, cultivation, collection, and properties of rubber, the treatment of the latex to convert it to crude rubber, the chemistry of rubber and its derivatives, including artificial rubber, the theory of vulcanization, the analytical methods of testing, the physics of rubber, and the physical methods of testing.

The work is replete with statistics, scientific data, and descriptions of methods which are of great value to all of those interested in any aspect of rubber production or treatment. The theories of the structure of rubber, of its polymerization, of vulcanization, of rubber as a disbursing medium, are all of great interest to the physical chemists as well as to organic chemists and chemical engineers. In fact any scientist not already familiar with the science and properties of rubber is sure to find new ideas extending into many different fields of physics and physical chemistry.

In preparing this translation for the English reading public, a valuable service has been rendered in a very acceptable manner. The translators have made such additions and corrections in the way of footnotes as were necessary to make the work clear and to bring it up to date. They have checked the literature references and added an unusually well arranged and classified bibliography covering the entire subject. The work appears indispensable to all those interested in any of the scientific phases of rubber.

S. C. LIND.

Physical Chemistry. By A. J. MEE. 14 x 22 cm.; xix + 780 pp. London: William Heinemann, Ltd., 1934. Price: 15s.

"This book," the author states, "sets out to give an up-to-date outline of the results and methods of Physical Chemistry. . . . The book is suitable for students who are preparing for the Higher School Certificate and Intermediate Science Examinations of the various Universities, for University Scholarships, and for University degrees up to Pass standard." In achieving the end which he had in view, the author has been very successful. In the book under review, we have a well-written and clear discussion of a wide range of topics, "all the topics usually dealt with under the heading of Physical Chemistry," as the author assures us, including photochemistry and the methods used in determining the structure of the simpler molecules; and any student who masters this work will have a knowledge of physical chemistry which should carry him well beyond the standard for a Pass degree. Mr. Mee has given, on the whole, a remarkably clear and comprehensive survey of the whole range of physical chemistry, and he has taken pains to keep the mathematical treatment and the explanation of physical concepts as simple as is consistent with an exact treatment of the subject. Sometimes, it is true, one feels that rather too great a comprehensiveness has been attempted and that the book may too easily lead to "cramming" on the part of the student. Useful summaries are given at the end of each chapter, together with a list of books and memoirs for further reading and a large number of questions and problems by which the student can test his mastery of the subject. The book is a readable and trustworthy introduction to physical chemistry and should serve very well the purpose for which it was written.

ALEX. FINDLAY.

The Nitrogen System of Compounds. By EDWARD CURTIS FRANKLIN. American Chemical Society Monograph No. 68. 23 x 15 cm.; 339 pp.; 26 figs.; 12 tables. New York: Reinhold Publishing Corp., 1935. Price: $7.50.

Nitrogen is unique among the elements in the multiplicity of types of chemical combinations into which it enters and in the diverse reactions which it exhibits. Nitrogen compounds have long been the object of many excellent and painstaking researches, and numerous volumes have been written on the subject of nitrogen chemistry. Yet withal no single point of view has been set forth so far which is sufficiently broad and simple to realize a systematic classification of their reactions. The simplest and most powerful tool which has been proposed for the accomplishment of the above ends is that of the "nitrogen" system of compounds formulated by E. C. Franklin and developed by him and his students. The present monograph embraces the life-long work of Professor Franklin and summarizes a unique American development of chemical thought.

Professor Franklin states that "the object of this monograph is to outline what we have chosen to call the nitrogen system of compounds and to bring to the attention of chemists the remarkable extent to which the compounds of nitrogen simulate in their properties and behavior the analogous compounds of oxygen." This purpose is kept paramount throughout the work. So also are the general objectives set for the A. C. S. monograph series.

The essential idea of the "nitrogen" system (more frequently referred to as the "ammonia" system) is a simple one. Granting the dominating rôle played by oxygen in a majority of the more familiar types of chemical compounds (a relationship clearly expressed by Laviosier), the contention is that nitrogen similarly conditions the behavior of an equally large number of compounds. We are less familiar with the latter because of the natural abundance of water on this planet and of the chemist's long enslavement to the use of water as a solvent and reaction medium. Impressed by the marked similarity between the physical and chemical properties of liquid ammonia and water, Franklin early sought to show that this resemblance extends to the derivatives of these two substances. In this manner he established two systems of compounds, an oxygen (or water) system and a nitrogen (or ammonia) system, and showed experimentally that the corresponding members of both systems possessed similar physical properties and took part in essentially the same kind of chemical reactions. For the sake of clarity and emphasis, Franklin found it necessary to devise a nomenclature which would portray the behavior of nitrogen in the reactions of its compounds as the existent nomenclature so well portrayed the similar behavior of oxygen in the reactions of its compounds. Hence the use of the terms ammonation, deammonation, nitridation, ammonolysis, ammolytic, etc.

With no thought of describing the behavior of the various representatives of the nitrogen system, it is well to note that one finds ammonates, ammono acids, bases and salts, acid anammonides, basic nitrides, ammonobasic salts, and salts of amphoteric amides whose chemical behavior closely parallels that of the oxygen compounds of the corresponding type. Further there are many substances which belong at the same time to the nitrogen and oxygen systems, the nitrogen and sulfur systems, etc. A unique and significant contribution of the concept of a nitrogen system of compounds is the classification and correlation which it provides for the so-called mercuriammonia compounds. The same concept is of tremendous value among organic compounds in its systematization of the chemistry of such a wide variety of materials as the amines (ammono alcohols and ethers), aldimines (ammono aldehyde-alcohols), ketimines (ammono ketone-alcohols), and hydramides (ammono aldehyde-acetals), Schiff's bases (ammono aldehyde-ethers and ammono ketone-ethers), amidines (ammono carboxylic acids), nitriles (carboxylic acid anammonides), isocyanides (esters of ammonocarbonous acid), cyanamide and guanidine (ammonocarbonic acids), nitrosoamines and diazo compounds (derivatives of ammono- or aquo-ammononitrous acids), and the nitrogen heterocycles such as pyridine (cyclic ammono aldehyde-ether). It might be argued that any concept based on analogy carries with it certain elements of weakness. Yet when this argument is applied to the concept of systems of compounds it loses much of its significance because the extreme fruitfulness of the concept is sufficient evidence of its strength.

As a presentation of exciting knowledge in its field, the book is remarkably complete and contains considerable material not otherwise readily available. There can be no question that this book will greatly stimulate research in the field of nitrogen chemistry. Already the chemical literature gives ample evidence of the influence of Franklin's ideas. Not only are investigators following his lead in interpreting reactions of nitrogen compounds according to the nitrogen system, but they are also proposing other systems of compounds to correlate behavior for substances other than those containing ammonia nitrogen.

There seems to be only one factor which is likely to hinder the great usefulness of this monograph—the price asked for it prevents many students from realizing their desire to own it.

A very desirable feature of the book is the appendix on the experimental manipulation of liquid ammonia solutions. It is to be hoped that we may soon have available a compilation of existing data relative to liquid ammonia solutions to supplement Professor Franklin's monograph on the nitrogen system.

W. CONARD FERNELIUS.

Colloidal Electrolytes. A general discussion held by the Faraday Society. 16 x 25 cm.: 421 pp. London: Gurney and Jackson, 1935. Price: 18s. 6d.

The volume contains thirty-six main contributions to the subject, originating from twenty different universities and research institutes distributed throughout ten European countries and the United States, and a considerable amount of critical discussion in which other schools of research are represented. Such variety and number has naturally necessitated a very wide meaning being attached to the title. In consequence this, the largest of the Faraday discussion volumes yet published, will probably be less easily comprehensible as a whole to individual workers in the field than its forerunners. It should all the more prove extremely useful to them, since at least half the matter in it will be immediately relevant to any one interested, and the remainder may prove more relevant than might at first appear. The book will therefore be a stimulus as well as a work of reference to recent progress.

The subject is divided broadly into a general part and a special and technical part. The former comes mainly under the heading of theory, but includes also a short section on experimental methods. The latter is divided into five headings: (a) soaps and other long-chain electrolytes, (b) dyes, (c) silicates, (d) proteins, and (e) other substances. In the theoretical section thermodynamic and electrical properties are discussed from the points of view of electrolyte and surface theory, and under the special headings biological and industrial applications, as well as the special properties of the substances concerned, are described. The absence of any general summary of the work of McBain and collaborators, who contribute, however, two special papers, will disappoint those interested in soap-like substances, but on the whole the book is very well balanced and the society and its editor are certainly to be congratulated on their achievement.

The binding in boards is an improvement on the old paper covers but is still insufficiently strong for a book which should find so much use.

G. S. HARTLEY.

Reports on Progress in Physics. Published by the Physical Society. 25 x 18 cm.; iv + 371 pp. Cambridge: Cambridge University Press, 1934. Price: 12s. 6d. net to non-fellows.

This is the first volume of a series of annual reports to be issued by the Physical Society, and it sets a very high standard for the future. It is a well printed and strongly bound volume of attractive appearance, and the contents range over several important branches of physics. Quantum mechanics and wave mechanics (Temple); the spiral nebulae and the expansion of the universe (McVittie), and Burgers' theory of turbulence (Trubridge) appeal to the mathematical physicist. Articles on surface tension (Ferguson), sound (E. G. Richardson), spectroscopy (in twelve sections, including one on wave length standards, by R. W. B. Pearse, H. Dingle, E. Gwynne-Jones, C. V. Jackson and A. Hunter), optics (by T. Smith, J. S. Anderson, J. Guild, and H. F. Buckley, all of the National Physical Laboratory), heat (by J. H. Awbery, of the same laboratory) and electric and magnetic measurements (L. Hartshorn) are all highly practical and competent surveys of the modern position of each subject, not confined to very recent work and not at all mere abstract summaries but real authoritative monographs full of valuable information. Sections on electrical phenomena at extremely low temperatures (McLennan) and the physics of the atom (Andrade) are perhaps the outstanding features of the volume, since they survey in a lucid and masterly way the whole aspect of each subject, and each gives a coherent picture of the position at the time of writing—now, it is true, already somewhat modified. A pleasing feature of the whole volume is the insistence on experimental method: good diagrams of apparatus, tables, and curves are given, and an overinsistence on certain aspects of very modern physics has been successfully avoided by a wise choice of authors. The volume is one which every physical chemist should possess.

J. R. PARTINGTON.

FACTORS INFLUENCING ELECTROPHORETIC MOBILITIES AND APPARENT CRITICAL POTENTIALS

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Various observers have reported that electrophoretic mobility is increased above the water value by the addition of uni-univalent salts. Powis (16) found the mobility of oil droplets to increase with added potassium chloride up to 2.5×10^{-3} *M* and then to fall off. He also found (17), according to his table 1, that clouding of an oil emulsion after two days begins in 5×10^{-3} *M* potassium chloride, where the zeta potential is 52 mv. or electrophoretic velocity is 3.7μ per second per volt per centimeter, the zeta potential in water being 46 mv. With barium chloride, clouding after two days begins in 5×10^{-4} *M*, with a zeta potential of about 37 mv.; with aluminum chloride in 1×10^{-5} *M* with a zeta potential of 38 mv.; and with thorium chloride between 5×10^{-6} and 1×10^{-5} *M* with a zeta potential between 40 and 7 mv. However, Powis rather arbitrarily takes a break in the clouding–concentration curve as the criterion of the critical condition, this occurring in all cases at a higher concentration than that required to initiate clouding. At these critical concentrations so defined, the zeta potential is about the same with all the salts investigated, that is, close to 30 mv., which is taken as the critical potential.

Powis (18), working with arsenic trisulfide sol, took the conditions obtaining in 5×10^{-4} *M* barium chloride as critical. Here coagulation is rapid and the zeta potential is 26 mv. The same degree of coagulation was first obtained in aluminum chloride at 5×10^{-5} *M* with a zeta potential of 25 mv. and in 7×10^{-5} *M* thorium nitrate with a zeta potential of 26 mv. The zeta potential with the "pure" colloid was not determined, but he concludes that it would be less than 100 and probably less than 60 mv. With potassium chloride, however, the critical concentration was 4×10^{-2} *M* and the zeta potential 44 mv. Powis ascribes the higher critical potential in potassium chloride to a salting-out effect due to the higher concentration required with univalent salts, i.e., the sol would still have been stable at a zeta potential of 44 mv., but for the salting-out effect.

Kruyt and van der Willigen (9), working with arsenic trisulfide, selenium, and mercuric sulfide sols, do not carry the mobility–concentration curves quite out to the flocking concentrations, but it is evident that with all the sols mobility at flocking concentration of uni-univalent salts is greater than for salts with bivalent cations. With the former salts the mobility usually increases continuously almost up to the flocking concentration. They conclude that electrophoretic mobility is not a true measure of zeta. They ascribe the increasing mobility with increasing concentration of univalent salts up to nearly the flocking concentration and the fact that mobility at flocking concentration is higher with univalent than with multivalent cations to (1) variations in dielectric constant produced by the relatively high univalent salt concentration required for flocking (3 to 8 × 10^{-2} M) and to (2) the probable incorrectness of the assumption that the mean distance between the electrical double layers equals the distance from the wall at which fluid velocity becomes constant. As to the first of these points, considerable difference of opinion exists regarding the effect of added electrolytes on the dielectric constant of water; the effect postulated by Kruyt may exist but cannot at present be evaluated quantitatively (10). As to the second point, Koenig (6) has pointed out that this assumption is not essential to the derivation of the electrokinetic equations. The above results were obtained with an ultramicroscopic method. Kruyt and Tendeloo (8) also find the mobility of lyophilic sols increased on addition of electrolytes, using a moving boundary method. However, in a later paper Bungenberg de Jong, Kruyt, and Lens (2) question the earlier results, showing increased mobility in presence of electrolytes, and state that unpublished results of Kruyt and de Haan with a microscopic method show no such increase, the implication of this last paper apparently being that electrophoretic determinations properly carried out are a true index of zeta.

Pennycuick (14) found the mobility of platinum sols to increase slightly in low sodium chloride concentrations and then to fall off slowly, being at the coagulating concentration about 80 per cent as great as in water. The critical mobility, i.e., that at the coagulating concentration, was about the same for barium chloride, barium hydroxide, and hydrochloric acid and was about half as great as the critical mobility in sodium chloride; the critical concentrations for barium chloride were much lower than for sodium chloride, the latter being about 3 × 10^{-3} M.[1]

Similar results with various sols have been reported by Ivanitzkaja and Proskurvin (5),[2] by Briggs (1), and by various other workers. Freundlich and Zeh (3), however, find only a decrease of mobility of arsenic trisulfide sol on adding potassium chloride or other univalent salts; they used the moving boundary method. Rabinowitsch and Fodimann (19) find that addition of potassium chloride decreases mobility of arsenic trisulfide sols if the acid content of the sol is low and increases it if the acid content is high; their results seem surprising in that after adding 7×10^{-4} *M* hydrochloric acid, additional 2×10^{-5} *M* potassium chloride exerts a significant effect.

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[1] The concentration figures of figure 2 of this paper are apparently all too low by tenfold, evidently a typographical error; compare Pennycuick (Z. physik. Chem. **148**, 419, 424 (1930)).

[2] The results in their very dilute solutions, as with 1 × 10^{-11} M potassium chloride added, can hardly be of any significance.

Various explanations for the increasing electrophoretic mobility on addition of uni-univalent electrolytes have been proposed. Powis (18) believes that it is due to an actual increase in zeta, effected presumably by an increase in the charge density by adsorption of added anions. The later fall in mobility in the higher concentrations would then be ascribed to a lessened diffuseness of the positive layer with a resultant lowering of zeta. That the higher critical mobility with univalent inorganic salts is dependent on the high concentrations required for coagulation is shown by the results of Briggs (1) with highly adsorbed univalent organic cations. With these coagulation is produced in low concentrations, and the critical mobility is that common to all polyvalent cations. With the monovalent inorganic potassium cation Briggs agrees with other workers in finding an initial increase in mobility which may be back to normal in 5×10^{-3} *M*. Briggs accepts the view of Kruyt and van der Willigen (7) that the maintained or increasing mobility in relatively concentrated uni-univalent inorganic electrolyte solutions is due to an increase in dielectric constant rather than in zeta. Rabinowitsch and Fodimann could not consistently verify Freundlich and Zeh's prediction, which was based upon a concept developed by Hevesy (4) that if the original zeta potential is greater than 70 mv., addition of electrolytes will lower it to 70, while if the original value is less than 70, electrolytes will raise it to 70. Rabinowitsch and Fodimann's explanation of the salt effect appears to be self-contradictory. They first say that the chief factor lowering zeta is the replacement of hydrogen ions in the electrical layer by potassium ions; this occurs in their non-acidified sols with a resultant lowering of mobility. This replacement is inhibited by an increased acidity of the medium, and therefore with an acidified sol the addition of potassium chloride does not lower the zeta potential or mobility. In the next paragraph, however, to explain the actual increase in mobility often seen in acidified sols on addition of potassium chloride, they assume that potassium ions form a more diffuse layer than hydrogen ions with a resultant increase in zeta.

Pennycuick (14, 15) assumes that the strong affinity of the platinum surface for hydroxyl groups causes a hydrolytic cleavage of the salt, the basic cleavage product then reacting at the surface to form new ionogenic spots. It is difficult to accept this explanation, however, since the addition of a neutral salt to water does not increase the hydroxide-ion activity.

In any case Pennycuick makes no attempt to explain the finding that the critical mobility with bases and neutral monovalent salts is higher than with salts of polyvalent cations.

In a previous publication (White, Monaghan, and Urban (22)) it was shown that in water and dilute solutions the ratio of electrosmotic velocity on a plane Pyrex surface to electrophoretic velocity of Pyrex particles 1 to 3μ in diameter was always greater than unity. The ratio decreased as the concentration of added salt increased, becoming unity at a concentration between 10^{-3} and 10^{-2} M potassium chloride and at all higher concentrations. Although values for the absolute magnitude of electrokinetic velocity were not obtained at that time, it was pointed out that the discrepancy in the ratio was undoubtedly to be ascribed to retardation of the particles in dilute solutions. Several factors were assumed to be responsible for this retardation. Two of these, the decrease of (1) double layer thickness and (2) charge density, with decreasing particle radius, retard the particle by lowering the zeta potential. This effect is present whether or not an external voltage is applied; it will therefore contribute to the instability of the particle. A third factor, the distortion of the electric field by the particle, is of doubtful significance in the case of the conducting particles of metallic sols. The fourth factor, however, the polarization of the diffuse double layer by the external field, which was considered most important in causing deviation of the ratio from unity, applies to all particles in dilute solutions. Zeta, calculated from electrophoretic velocity, will therefore be considerably lower than the electrosmotic zeta, lower also than the true zeta of the particle. Furthermore, it will appear to go through a maximum on the addition of salt when no maximum exists in the electrosmotic or true zeta–concentration curves.

The bearing of these findings on the problem of critical potentials of lyophobic sols is obvious. Those salts which coagulate at low concentrations will appear to have a lower critical potential (measured by electrophoresis) than the monovalent salts and bases which require much higher concentrations to precipitate. This apparently lower critical potential is, however, an artifact inherent in the electrophoretic method.

It is difficult to obtain electrosmotic measurements on surfaces identical with the colloidal sols used in coagulation studies. On the other hand, both electrosmotic and electrophoretic data may easily be obtained on glass and protein-coated glass surfaces. The present paper is concerned with the absolute magnitude of electrosmotic and electrophoretic velocities on glass and protein-coated surfaces as a function of electrolyte concentration.

EXPERIMENTAL

Both electrophoretic and electrosmotic velocities were obtained by observing microscopically the movement of particles at stated levels in a

Pyrex electrophoresis cell of the type described by Mattson (11). It follows from the formula expressing electrosmotic flow of the liquid at different levels in a cylindrical cell (Mattson (12)) that true electrophoretic velocity in such a cell is the observed velocity of the particles at 0.147 of the diameter from the wall. True electrosmotic velocity is the velocity of the water immediately adjacent to the wall, or (with reverse sign) that of the water in the center of the cell. It may be obtained by subtracting algebraically the true electrophoretic velocity from the observed velocity of the particles either at the wall or in the center of the tube. Both methods were used in the present experiments and gave good agreement.

TABLE 1

Potassium chloride-Pyrex at 37°C.

CONCENTRATION OF KCl	μ/SEC TOP	μ/SEC MIDDLE	V_p = μ/SEC AT 0 147	V_w μ/SEC ($V_p + V_{top}$)	V_w μ/SEC ($V_{middle} - V_p$)	V_w μ/SEC AVERAGE	$\frac{V_p}{V}$ /CM	$\frac{V_w}{V}$ /CM	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar											
H_2O	−44 6	+78 8	+15 9	60 5	62 9	61 7	3 49	13 6	35	134	3 8
10^{-5}	−41 7	+73 3	+15 5	57 2	57 8	57 5	3 41	12 6	34	124	3 7
10^{-4}	−29 8	+66 7	+18 6	48 4	48 1	48 3	4 09	10 6	40	105	2 6
10^{-3}	−13 7	+59 9	+22 7	36 4	37 2	36 8	4 99	8 09	49	80	1 6
10^{-2}	0	+46 1	+23 5	23 5	22 6	23 0	5 16	5 05	51	50	0 98

TABLE 2

Potassium chloride-Pyrex

CONCENTRATION OF KCl	AT 25°C					AT 32°C.				
	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec / v /cm*	*μ/sec / v /cm*				*μ/sec / v /cm*	*μ/sec / v /cm*			
H_2O	3 49	11 8	38	130	3 4	3 65	11 2	46	141	3 1
1×10^{-5}	3 14	9 59	35	105	3 0	3 45	10 8	43	136	3.2
1×10^{-4}	3 54	9 12	39	100	2 6	3 54	9 74	45	123	2.7
5×10^{-4}	4 04	8 15	44	90	2 0	4 26	8 33	54	105	1 9
1×10^{-3}	4 39	7 10	47	78	1 7	4 62	7 61	59	96	1 6
1×10^{-2}	4 77	3 89	52	43	0 83	4 13	4 13	52	52	1 0
1×10^{-1}						2 24	2.24	28	28	1 0

Table 1 contains the results of a typical experiment showing the effect of varying concentrations of potassium chloride on the electrophoretic mobility of Pyrex particles and the electrosmotic velocity at a Pyrex surface. Glass-distilled water with a conductivity of 1 to 1.5 × 10^{-6} mhos was used throughout. The particles were obtained by pulverizing Pyrex tubing in a porcelain mortar. A fairly uniform stock suspension of particles about 1μ in diameter was obtained by fractional sedimentation. The

TABLE 3

Hydrochloric acid–Pyrex at 36°C.

CONCENTRATION OF HCl	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec./v./cm.*	*μ/sec /v /cm.*			
H_2O	2.64	10.1	26	101	3.9
10^{-5}	3.34	12.1	33	121	3.7
10^{-4}	3.63	6.02	36	60	1.7
10^{-3}	3.58	4.11	36	41	1.1
10^{-2}	2.31	2.20	23	22	0.96

TABLE 4

Potassium ferrocyanide–Pyrex at 27°C.

CONCENTRATION OF $K_4Fe(CN)_6$	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec /v./cm*	*μ/sec./v./cm*			
H_2O	2.97	10.1	36	121	3.4
10^{-6}	3.01	7.50	36	90	2.5
10^{-5}	3.43	7.30	41	88	2.1
10^{-4}	4.33	6.68	52	80	1.5
10^{-3}	4.68	4.68	56	56	1.0

TABLE 5

Sodium hydroxide–Pyrex at 25°C.

CONCENTRATION OF NaOH	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec /v /cm.*	*μ/sec /v /cm*			
H_2O	2.44	8.18	31	103	3.3
10^{-5}	3.01	9.30	38	117	3.1
10^{-4}	3.56	12.3	45	155	3.4
10^{-3}	4.44	10.3	56	130	2.3
10^{-2}	5.95	6.83	75	86	1.1

TABLE 6

Potassium sulfate–Pyrex at 25°C.

CONCENTRATION OF K_2SO_4	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec /v /cm*	*μ/sec /v /cm.*			
H_2O	3.38	9.80	43	123	2.9
10^{-5}	3.58	9.43	45	119	2.6
10^{-4}	4.46	8.48	56	107	1.9
10^{-3}	5.45	7.00	69	88	1.3
10^{-2}	3.12	2.84	39	36	0.92

cell was allowed to stand in chromic acid cleaning solution between experiments. The voltage across the cell was 116 volts, giving a field strength of 4.55 volts per centimeter. V_p represents true electrophoretic velocity; V_w the true electrosmotic velocity. The sign refers to the electrode toward which the particles were observed to move at the levels indicated. The zeta values were calculated from the well-known formula:

$$\zeta = \frac{4\pi V\eta}{ED}$$

where V = velocity, η = viscosity, E = field strength, and D = dielectric constant. The room temperature at which the experiments were performed is given for each experiment.

TABLE 7

Potassium chloride-gelatin at 38°C.

CELL	CONCENTRATION OF KCl	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
	molar	*μ/sec /v /cm*	*μ/sec /v /cm*			
Flat cell	H_2O	1.94	3.34	19	32	1.7
	10^{-5}	2.07	3.64	20	32	1.6
	10^{-4}	1.90	2.78	18	25	1.4
	10^{-3}	1.75	1.84	17	19	1.1
	10^{-2}	0.94	0.98	9.1	9.5	1.04
Cylindrical cell	H_2O	1.58	3.54	15	34	2.3
	10^{-5}	1.69	3.43	16	33	2.1
	10^{-4}	1.80	3.38	18	33	1.8
	10^{-3}	1.56	2.22	15	22	1.5
	10^{-2}	1.01	1.01	9.8	9.8	1.0

In tables 2 to 7 only the velocities and the calculated zeta values are given. Table 2 contains the results of two additional experiments on potassium chloride. Some variations in velocity at a given concentration, especially in water and the more dilute solutions, are perhaps to be expected, considering the great effect which small amounts of contaminating substances may exert on the surface potential of glass. Tables 3 to 6 show the effect of various other electrolytes on glass.

Table 7 gives the results of two experiments on gelatin-coated glass surfaces in varying concentrations of potassium chloride. Each solution contained $\frac{1}{10}$ g. per liter of gelatin, a concentration sufficient to coat the glass completely with a protein film. No attempt was made to regulate the pH. The first set of readings was obtained with a flat electrophoresis cell of the Northrop-Kunitz type. The field strength was determined in each solution from measurements of the current and the conductivity of the solution. The experiment was then repeated, using the cylindrical Mattson cell. Since the gelatin itself contained a considerable amount of electrolyte (the specific conductivity of the gelatin solution in distilled water was 5.4×10^{-6} mhos, corresponding roughly to that of a 2×10^{-5} *M* potassium chloride solution) the addition of small amounts of potassium chloride had little effect on either electrophoretic or electrosmotic velocities.

DISCUSSION

It will be seen from the tables that, with the exception of sodium hydroxide, all the electrolytes investigated, including the tetravalent $Fe(CN)_6$ anion, reduce the electrosmotic velocity at the glass–water interface. Similar results were obtained by Powis (16) with electrosmosis and by Kruyt and van der Willigen (9), using the stream potential method on glass capillaries. In spite of the fact that zeta is decreasing, the electrophoretic velocity increases continuously up to concentrations of about *M*/100 for the uni-univalent electrolytes. Since the main factor (polarization of the double layer by the impressed field) discussed in our previous paper (22), which is responsible for the retardation of the electrophoretic mobility of glass particles, applies equally well to all particles in dilute solutions, it may be inferred that the metallic sols studied by Pennycuick, Briggs, Kruyt, and others have a higher potential in dilute solutions than that calculated from their electrophoretic mobility. The true zeta potential can be measured by the electrophoretic method only in relatively concentrated solutions, about *M*/100 or more. When large concentrations of electrolyte are required for precipitation, as is the case with inorganic uni-univalent salts and bases, the electrophoretically measured critical potential probably represents approximately the true zeta potential of the particle at the coagulation point. This is not the case, however, for the acids and polyvalent cations which precipitate in concentrations so small that polarization of the double layer may occur; here the electrophoretically measured critical potential is lower than the true zeta potential of the particle at that concentration.

The explanation of Powis (18) for the higher critical mobility (which he considers as evidence for higher critical potential) with inorganic uni-univalent salts than with multivalent salts is that of a salting-out effect which lowers the stability of the particles without lowering zeta. It seems improbable to us, however, that such a low concentration as 5×10^{-3} *M* potassium chloride could exert any significant effect of this type. The same statement applies, as pointed out by Weiser (21), to Kruyt's postulated changes in dielectric constant. The changes in dielectric constant with added potassium chloride are about 2 to 3 per cent as the salt concentration is increased from 0 to *M*/100 (Pechold (13); Walden and Werner (20)), whereas the variations in electrophoretic mobility are of the order of

50 per cent. It is, of course, possible to postulate greater deviations in the dielectric constant within the double layer itself, but such assumptions cannot be investigated experimentally. The point to be emphasized in the present paper is that no such assumptions are necessary to account for the facts that electrophoretic mobility (1) increases with increasing salt concentration, and (2) is lower at the critical concentration of the salts of polyvalent cations than it is at the much greater critical concentration of potassium chloride; an adequate explanation is to be found in the retardation of electrophoretic mobility in dilute solutions, which has here been experimentally demonstrated.

SUMMARY

The electrophoretic mobility of small glass particles is found to be much less than the electrosmotic mobility at a glass surface in dilute electrolyte solutions, whereas the mobilities are identical in solutions of concentration $M/100$; the same holds for gelatin surfaces. This is believed to be due to a retardation of the particles in dilute solutions, chiefly because of the polarization of the double layer by the applied field. On this basis the increase in electrophoretic mobility (with increasing concentrations of neutral univalent salts) while electrosmotic mobility is decreasing is explained. Also, the apparently lower critical potential obtained with electrolytes which coagulate in low concentrations as compared with those which require higher concentrations is considered to be an artifact, due to the impossibility of calculating the zeta potential from electrophoretic mobility in dilute solutions. It is thus concluded that the mobilities of particles in critical concentrations of polyvalent salts are abnormally low, rather than, as has usually been assumed, that the critical potentials with inorganic monovalent salts are abnormally high. According to this concept the critical mobility in inorganic monovalent salt solutions is a true measure, while the true zeta potential in the critical concentrations of polyvalent salts is higher than that indicated by mobility and may be the same as that with inorganic monovalent salts. The often reported finding that the apparent zeta, as measured by electrophoresis, is higher in the critically flocking concentration of uni-univalent salts than it is in lower concentrations or in water, where the sol is stable, is given an explanation.

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A COMPARISON OF THE ELECTROKINETIC POTENTIALS AT FUSED AND UNFUSED GLASS SURFACES

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It has recently been shown (White, Monaghan, and Urban (6)) that the electrophoretic mobility of microscopic Pyrex particles is much less in dilute solutions than electrosmotic mobility in Pyrex cells. Since, however, the particles (prepared by pulverizing Pyrex tubing in a mortar) had broken surfaces, while the surface of the cell was fused Pyrex, the possibility remained that the observed discrepancies in electrophoretic and electrosmotic mobilities were due to differences in the adsorptive properties of fused and unfused surfaces rather than to differences in the phenomenon of electrophoresis as compared with electrosmosis. The object of the present paper is (1) to prepare fused Pyrex spheres 3μ or less in diameter and (2) to compare the electrophoretic mobility of such spheres with (a) the electrophoretic mobility of broken Pyrex particles and (b) electrosmotic mobility at fused Pyrex surfaces.

A method for the preparation of microscopic glass spheres has been described by Sklarew (4). A simpler and much less bulky apparatus for the preparation of small quantities of fused powder was designed with the help of J. H. Zimmer.[1]

The apparatus consists of a glass chamber, A, which holds the powder. A stirrer shaft, B, bearing a stirrer, C, which is beneath the powder, and wings, D, which agitate the air above the powder, is driven by an air turbine, E. The fine mist of glass powder is carried up through the alundum heating tube, F, and settles in the glass collecting chamber, G, which is covered loosely enough to allow escape of the air. The upward velocity of the particles depends upon the height of the heating tube, the extent to which it is heated, and the size of the air inlet, H. The collecting chamber is supported by a rod, I. A narrow section of the alundum tube is heated to white heat with an oxygen flame, the tube being heated and cooled gradually in order to prevent cracking. When the air intake is so adjusted that the particles move upward with a slow and uniform velocity, all of the particles up to 10μ in diameter are fused in passing through the heated portion of the tube and on microscopic examination are seen to be perfect spheres.

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[1] Departmental mechanic.

Both electrophoretic and electrosmotic measurements were carried out in a Pyrex electrophoresis cell of the type described by Mattson (1). In such cylindrical cells the water is at rest at a depth of 0.147 diameter from the wall (Mattson (2)); consequently the observed velocity of the particles at this depth is true electrophoretic velocity. Electrosmotic velocity of the water in the cell may be obtained by subtracting electrophoretic velocity from the observed velocity of the particles at the center of the cell. Both particles and cell were previously cleaned in chromic acid cleaning solution, the acid being removed by repeated washings in distilled water. The electrokinetic potential, ζ, was calculated from the well-known formula:

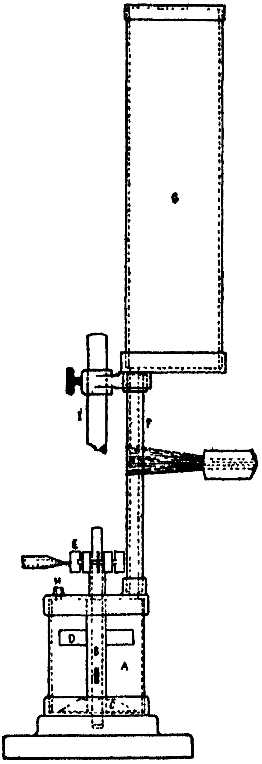

FIG. 1. APPARATUS FOR PREPARATION OF MICROSCOPIC GLASS SPHERES (× ¼)

$$\zeta = \frac{4\pi V\eta}{ED}$$

where V represents either electrosmotic or electrophoretic velocity, η the viscosity of the medium, E the applied field strength, and D the dielectric constant of the medium.

As a further check, electrosmotic experiments were also carried out on several Pyrex capillaries by the method described by Quincke (3). This consists in the measurement of the head of pressure developed by electrosmosis in a capillary of known radius under an applied E.M.F. A diagram of the apparatus is shown in figure 2. The Pyrex capillary, C, is connected by transparent rubber tubing to the open reservoir, R, and the closed vessel, V. Platinum discs, P, are sealed into the two arms of the apparatus close to the rubber connections so that practically all of the potential drop is across the capillary. Platinization of the electrodes permitted large currents to be used.[2] A larger capillary, the climbing tube T (about 1 mm. in diameter), is connected with the closed arm of the apparatus with rubber tubing. When a voltage is applied across the capillary C, the meniscus rises or falls in the climbing tube T according to the direction of the current. Since the cross section of T is very small with respect to that of R, the level of the liquid in R may be considered to be constant and the entire change in level takes place in T. The horizontal projection of the movement of the meniscus is measured by means of a microscope fitted with a calibrated scale in the eyepiece. The vertical height through which the liquid rises or falls for a given applied E.M.F. is the product of the tangent of the angle, a, which the climbing tube makes with the horizontal and the horizontal projection. The capillary C and the climbing tube T are thoroughly cleaned by heating in chromic acid before each determination. The electrokinetic potential is calculated from the formula:

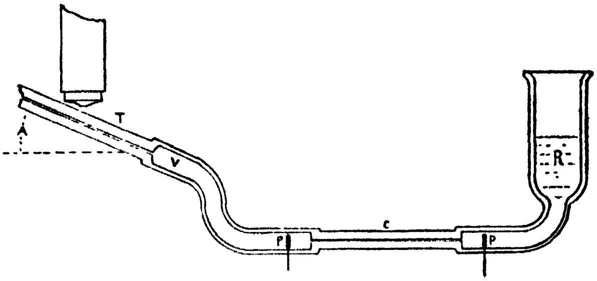

FIG. 2. APPARATUS FOR ELECTROSMOTIC MEASUREMENTS IN SINGLE GLASS CAPILLARIES

$$\zeta = \frac{P\pi r^2}{2HD}$$

where P is the pressure change, r the radius of the capillary C, H the total E.M.F. between electrodes, and D the dielectric constant.

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[2] In all experiments 350 volts were applied to the cell. This was conveniently supplied by a constant voltage "power pack," the output D.C. voltage showing fluctuations not greater than 0.01 volt. We are indebted to Dr. H. B. Peugnet of this department for the loan of this apparatus.

The results of electrophoresis and electrosmosis experiments in the closed cell are given in tables 1 and 2. V_p and V_w represent the velocity of the particles and the liquid, respectively, for an applied field of 1 volt per centimeter. The results show that, within the limits of experimental error, the fused Pyrex spheres move with the same velocity as the broken particles, and that the velocity of all the particles is less than electrosmotic velocity in solutions less concentrated than $M/100$. As previously stated (White, Monaghan, and Urban (6)) the discrepancy between electro-

TABLE 1

Electrophoresis of unfused Pyrex particles and electrosmosis at a fused Pyrex surface at 24°C.

CONCENTRATION OF KCl	V_p	V_w	ζ_p	ζ_w	$R = \frac{\zeta_w}{\zeta_p}$
moles per liter					
H_2O	3.4	10.0	44	130	2.9
H_2O	3.3	9.7	43	126	3.0
10^{-4}	3.4	7.6	44	99	2.2
10^{-3}	4.0	5.6	52	73	1.4
10^{-2}	3.1	3.0	40	39	0.98

TABLE 2

Electrophoresis of Pyrex spheres and electrosmosis at a fused Pyrex surface at 24°C.

CONCENTRATION OF KCl	V_p	V_w	ζ_p	ζ_w	$R = \frac{\zeta_w}{\zeta_p}$
moles per liter					
H_2O	3.1	8.6	40	112	2.8
H_2O	2.9	8.7	38	113	3.0
10^{-4}	3.2	7.3	42	95	2.3
10^{-3}	3.7	5.1	48	66	1.4
10^{-2}	3.0	3.1	39	40	1.02

TABLE 3

Electrosmotic zeta potentials of Pyrex capillaries

Quincke method

CONCENTRATION OF KCl	ZETA POTENTIAL						
	Capillary radius = 2.68 × 10^{-2} cm.			Capillary radius = 1.60 × 10^{-2} cm			Mean
moles per liter							
H_2O	102	109	114	103	112	123	111
10^{-4}	103	101	93	96	103	93	98
10^{-3}	92	78	85	86	80	80	83
10^{-2}	50			53	59	52	53

phoretic and electrosmotic velocities is believed to be due to a retardation of the particles because of several factors, chiefly the polarization of the diffuse double layer by the applied field.

Table 3 contains the electrokinetic potentials calculated from electrosmotic measurements by the Quincke method. Two capillaries of different radii were used. Three sets of determinations were made on each capillary, the determinations being made on different days with different samples of water. Each figure in the table represents the average of three determinations for each direction of current flow, these determinations agreeing among themselves within 10 per cent. It will be seen that the zeta potentials calculated from the Quincke method show satisfactory agreement with those obtained from electrosmosis in the closed cell, and are very much greater in dilute solutions than electrophoretic "zeta potentials." The rather wide discrepancy between the mean of the Quincke values in $M/100$ potassium chloride and the two values obtained for electrosmotic zetas in the closed cell is probably to be ascribed to experimental error rather than to any fundamental difference in the two methods. The means of several determinations of electrosmotic zetas in the closed cell reported elsewhere (White and Monaghan (5)) agree quite well with the values obtained here with the Quincke cell.

SUMMARY

1. A method is described for the preparation of microscopic glass spheres.
2. The electrophoretic velocity of Pyrex spheres is found to be the same as that of unfused Pyrex particles.
3. The electrophoretic velocity of Pyrex particles (fused or unfused) is much less in dilute solutions than electrosmotic velocity at a fused Pyrex surface, the latter being measured by two independent methods.

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JUNCTION POTENTIALS BETWEEN SOLUTIONS OF SUGARS AND POTASSIUM CHLORIDE

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The measurement of electrode potentials in sugar solutions has been frequently and advantageously employed by many workers to determine the pH of such solutions and to gain further insight into the oxidation-reduction behavior of the sugars. In making such measurements, potassium chloride salt bridges are almost universally used to connect the electrode in the sugar solution with the reference electrode,—a calomel half-cell, for instance.

Such procedure is not invariably safe. That is, if the sugar solution is too alkaline, or has been heated too much, or both, the solution may have present in it so high an ionic concentration that even a saturated potassium chloride salt bridge can not completely "smother out" the liquid junction potential. Urban and Shaffer have fully demonstrated that the junction potential between a saturated solution of potassium chloride and an even moderately alkaline solution of glucose is not a negligible quantity.

The purpose of this note is to present evidence that if the pH of the sugar solution does not greatly exceed 10, a saturated potassium chloride salt bridge may be relied upon to eliminate effectually all significant liquid junction potentials, no matter how concentrated the sugar solution may be. No attempt is made to explain the ionic mechanism involved in liquid junction potentials in general.

For the purposes of comparison, platinized platinum electrodes were immersed in two kinds of solutions, namely, normal hydrochloric acid and concentrated glucose. Both kinds of these solutions were connected to saturated calomel electrodes by potassium chloride salt bridges. Readings are given in table 1.

Columns 3 and 5 give the differences between the readings of the cells which included the stronger potassium chloride bridges and the reading of the cell with a 0.05 *N* bridge.

In the case of the solutions of *N* hydrochloric acid, there is seen to be a difference of 0.0167 volt between the readings of the cells with salt bridges of *N* and of 5 *N* potassium chloride. Such a difference may possibly be construed to mean that a greater concentration of potassium chloride than 5 *N*, if it could be prepared, would eliminate still more junction potential; namely, that even a saturated potassium chloride salt bridge fails appreciably to eliminate all the junction potential. Fales and Mudge, however, have expressed the belief that saturated potassium chloride bridges actually eliminate all but negligible junction potentials under these conditions.

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In considering column 5 in table 1, it is seen that the junction potentials involved in even concentrated glucose solutions of pH as high as 10 are much less than those for *N* hydrochloric acid. The reading for the saturated bridge is but little different from that of a *N* potassium chloride bridge. Since a fivefold increase in the concentration of potassium chloride produces only a small difference in the over-all reading of the cell, it seems reasonable to suppose that even a *N* potassium chloride bridge eliminates most of the junction potential and that a saturated bridge eliminates practically all of it.

TABLE 1

Over-all readings, in volts, of the various cells at 30°C.

(1) NORMALITY OF KCl IN BRIDGE	APPROXIMATELY NORMAL HCl		SOLUTIONS OF 60 G. GLUCOSE IN 100 CC BUFFER pH 10	
	(2) Readings	(3) Differences	(4) Readings	(5) Differences
0.05	0.3102	0	0.8527	0
0.10	0.3000	0.0102	0.8506	0.0021
0.50	0.2742	0.0360	0.8464	0.0063
1.00	0.2633	0.0469	0.8459	0.0068
5 (saturated)	0.2466	0.0636	0.8456	0.0071

Likewise we may assume that a solution of an infinite concentration of potassium chloride, if such were possible, could eliminate absolutely all such potential difference. In considering these data in the light of this assumption, we noticed that the values in column 5 fulfilled, within the limit of experimental error, the relationship demanded by the following equation:

$$Y = Y'10^{\frac{-K}{x-0.05}}$$

where Y = junction potential eliminated in excess of whatever is eliminated by a 0.05 *N* potassium chloride bridge. $Y = Y'$ when x, the concentration of potassium chloride, becomes infinitely large. K = a constant.

Since the above formula holds quite accurately throughout the range of all concentrations of potassium chloride that can be prepared, it is interesting to note that, according to this formula, the difference between the reading for a saturated bridge and the reading for a bridge of a concentration of potassium chloride of infinity is only 0.00016 volt. We therefore conclude that for the purposes for which most potential measurements are made on glucose solutions, the solution junction potential may be ignored when saturated potassium chloride salt bridges are used and the pH of the glucose solution does not greatly exceed 10, provided also that the sugar solution has not been heated or treated in any way that produces a large amount of ionized decomposition products.

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THE OXIDATION POTENTIAL OF THE SYSTEM POTASSIUM FERROCYANIDE-POTASSIUM FERRICYANIDE AT VARIOUS IONIC STRENGTHS[1]

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The oxidation potential of the ferrocyanide–ferricyanide system has been determined by a number of investigators (1, 3, 8, 9, 10, 11, 12, 13). After the introduction of the Debye-Hückel theory of strong electrolytes, this system becomes of special interest, since we are dealing here with highly unsymmetrical salts of high valence type. If potassium ferrocyanide and potassium ferricyanide behave like strong electrolytes, the oxidation potential should be greatly affected by a change of the ionic strength of the solution. In the first place, the purpose of this study was to determine the potential of the potassium ferrocyanide–potassium ferricyanide system at varying ionic strengths and to extrapolate the value to an ionic strength of zero; in other words, to determine the normal potential of the system. In addition, the potential of a very dilute ferro–ferricyanide solution was determined in the presence of different neutral salts at varying ionic strengths, in order to test the applicability of the Debye-Hückel equations.

At extremely small ionic strengths, the relation between the activity coefficient of an ion and the ionic strength of the solution is given by the expression:

$$-\log f = 0.5z^2\sqrt{\mu} \tag{1}$$

at 25°C. in water, in which z is the valence of the ion, and μ the ionic strength. The oxidation potential E of the system ferrocyanide–ferricyanide at 25°C. then is given by:

$$E = \epsilon_0 + 0.0591 \log \frac{a_{\mathrm{Fe_{ic}}^{---}}}{a_{\mathrm{Fe_{oc}}^{----}}}$$

$$= \epsilon_0 + 0.0591 \log \frac{c_{\mathrm{Fe_{ic}}^{---}}}{c_{\mathrm{Fe_{oc}}^{----}}} \cdot \frac{f_3}{f_4} \tag{2}$$

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[1] From the experimental part of a thesis submitted by William J. Tomsicek to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

The normal potential ϵ_0 denotes the potential referred to the normal hydrogen electrode in a system in which the activity of the ferricyanide $a_{Fe_{ic}^{---}}$ is equal to that of ferrocyanide $a_{Fe_{oc}^{----}}$. $c_{Fe_{ic}^{---}}$ and $c_{Fe_{oc}^{----}}$ represent the corresponding concentrations, whereas f_3 and f_4 represent the activity coefficients of the ferricyanide and the ferrocyanide ions. If the limiting Debye-Hückel expression (equation 1) holds at extremely small ionic strengths and the system contains equimolecular amounts of potassium ferricyanide and potassium ferrocyanide, it is found from equations 1 and 2 that:

$$E = \epsilon_0 + 0.0591 \log \frac{f_3}{f_4} = \epsilon_0 + 0.0591 \times 3.5 \sqrt{\mu} \qquad (3)$$

Therefore if the limiting Debye-Hückel expression holds, the measured potential E should change by 0.2068 volt for one unit change in the square root of the ionic strength.

The practical work in this study involves the use of a cell with liquid junction, the ferro–ferricyanide half-cell being measured against the quinhydrone electrode in a mixture containing 0.01 of an equivalent of hydrochloric acid and 0.09 of an equivalent of potassium chloride per liter, the saturated potassium chloride–agar salt bridge being used for making electrolytic contact between the two half-cells. No correction has been applied for the liquid junction potential, which is very small in dilute solutions containing potassium ferrocyanide and potassium ferricyanide, but may be greater in the presence of larger amounts of neutral salts. The introduction of the liquid junction potential, however, does not invalidate the conclusions arrived at in this paper.

EXPERIMENTAL PART

Materials used

$K_4Fe(CN)_6 \cdot 3H_2O$. A C.P. product of potassium ferrocyanide was recrystallized twice from conductivity water and kept over deliquescent sodium bromide hydrate. An analysis of the salt showed that it had the theoretical composition.

$K_3Fe(CN)_6$: A C.P. product of potassium ferricyanide was recrystallized twice from conductivity water and dried over anhydrous calcium chloride.

The various salts used in this work had been analyzed by W. Bosch and had been used in a previous study (4). Conductivity water was used throughout this work.

Apparatus and method for the measurement of the potential

The potential of the ferro–ferricyanide system was measured in a Pyrex cell as shown in figure 1, a piece of bright platinum gauze serving as electrode. One terminal of the potassium chloride–agar salt bridge was placed in the side well b, thus preventing diffusion of potassium chloride from the bridge into the main body of the solution. Nitrogen gas from a tank was introduced through c. Oxygen gas was removed from the nitrogen by passing the gas through electrically heated copper gauze at 500°C. The solution in the standard reference half-cell (0.01 *N* hydrochloric acid, 0.09 *N* potassium chloride saturated with quinhydrone) was prepared fresh every day. The normal potential of the quinhydrone electrode is 0.6990 volt at 25°C. Assuming that the paH of the acid mixture in the quinhydrone half-cell is equal to 2.075^5, we find that the potential of the latter against the normal hydrogen electrode is equal to 0.5764 volt at 25°C.[2]

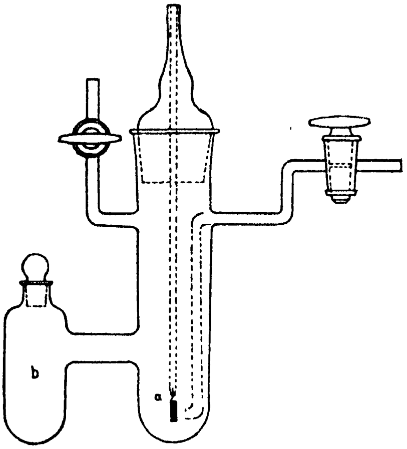

FIG. 1

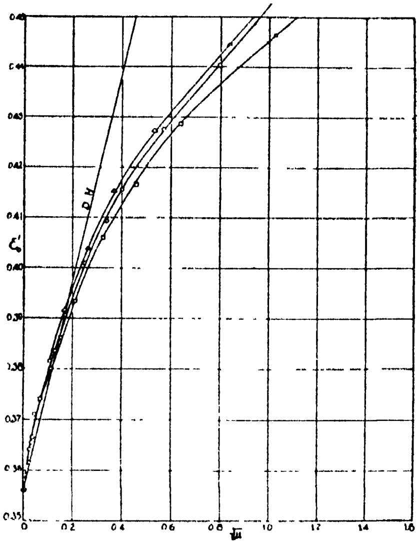

FIG. 2

FIG. 1. THE CELL

FIG. 2.

Ratio of $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$: ○, ratio 1:1; △, ratio 10:1; □, ratio 1:10. D. H., calculated from simple Debye-Hückel expression.

All the measurements were made in a thermostat at 25°C. ± 0.05°. Various salt bridges were used, all yielding the same values. The measurements were made with a Leeds and Northrup student potentiometer. For the dilution experiments a stock solution containing 0.1 *M* potassium ferrocyanide and 0.1 *M* potassium ferricyanide was carefully prepared by weight from the pure salts. This stock solution was kept in the dark and prepared fresh each day. The solutions from 0.1 to 0.004 molar were found to give the same potential in air as in a nitrogen atmosphere. The potential of the 0.004 molar solution in air referred to the normal hydrogen electrode was 0.4009 volt after 5 minutes and 0.4011 volt after 60 minutes. The same solution in a nitrogen atmosphere gave readings of 0.4011 and 0.4012 volts after 5 and 60 minutes respectively. More dilute solutions gave higher readings in air than in nitrogen. The potential of the 0.0004 molar solution was measured at least ten times during the course of the investigation. In a nitrogen atmosphere, the values found after 5 minutes remained unchanged for periods of twelve hours and more. The various readings agreed within ±0.0003 volt, the average being 0.3754 volt. The reproducibility of measurements with solutions from 0.0004 to 0.00006 molar was within 0.0005 volt. Each of the solutions was prepared fresh and measured at least four times.

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[2] Recently Guggenheim and Schindler (J. Phys. Chem. **38**, 533 (1934)) gave evidence that the paH of the standard acid mixture used in the quinhydrone electrode is equal to 2.10.

TABLE 1

Oxidation potential of equimolecular mixtures of potassium ferrocyanide and potassium ferricyanide

M	μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)
0.1*	1.6	1.265	0.1178	0.4586
0.04	0.64	0.8	0.1362	0.4402
0.02	0.32	0.5657	0.1490	0.4276
0.01	0.16	0.4	0.1610	0.4154
0.007	0.112	0.334	0.1670	0.4094
0.004	0.064	0.253	0.1753	0.4011
0.002	0.032	0.173	0.1856	0.3908
0.001	0.016	0.1265	0.1930	0.3834
0.0008	0.0128	0.1131	0.1950	0.3814
0.0004	0.0064	0.08	0.2010	0.3754
0.0002	0.0032	0.0566	0.2050	0.3714
0.0001	0.0016	0.04	0.2100	0.3664
0.00008	0.00128	0.0358	0.2112	0.3652
0.00006	0.00096	0.031	0.2122	0.3642
0.00004	0.00064	0.0253	0.2145	0.3619

* M = 0.1 designates that the concentrations of both potassium ferrocyanide and potassium ferricyanide are equal to 0.1 mole per liter.

Light was found to have a distinct effect on solutions whose concentrations were 0.0004 M or less, the E.M.F. tending to increase in light. All measurements were therefore made in a darkened room. Under these conditions, the potentials of even the most dilute mixtures remained constant for at least one hour.

Experimental results

Table 1 gives the average of the results of measurements with equimolecular mixtures of potassium ferrocyanide and potassium ferricyanide, μ representing the ionic strength. The value of ϵ_0 was found by plotting the measured values of E against $\sqrt{\mu}$ on large cross section paper and extrapolating to an ionic strength of zero. It was found to be equal to 0.3560 volt. The data are plotted in figure 2. The straight line represents the change of E, assuming that the limiting Debye-Hückel expression holds (equation 3).

TABLE 2

Oxidation potentials measured in a mixture containing $K_3Fe(CN)_6$ *and* $K_4Fe(CN)_6$ *in the ratio 10:1*

$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	TOTAL μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)	ϵ'_0 CALCULATED
M	*M*					
0.1	0.01	0.7	0.8366	0.0723	0.5041	0.4450
0.04	0.004	0.28	0.529	0.0898	0.4866	0.4275
0.02	0.002	0.14	0.3742	0.1020	0.4744	0.4153
0.01	0.001	0.07	0.2646	0.1130	0.4634	0.4043
0.004	0.0004	0.028	0.1673	0.1258	0.4506	0.3915
0.002	0.0002	0.014	0.1183	0.1337	0.4427	0.3836
0.001	0.001	0.007	0.0837	0.1398	0.4366	0.3775
0.004	0.00004	0.0028	0.0530	0.1462	0.4302	0.3711

TABLE 3

Oxidation potentials measured in a mixture containing $K_3Fe(CN)_6$ *and* $K_4Fe(CN)_6$ *in the ratio 1:10*

$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	TOTAL μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)	ϵ'_0 CALCULATED
M	*M*					
0.01	0.1	1.06	1.0295	0.1895	0.3869	0.4460
0.004	0.04	0.424	0.6511	0.2068	0.3696	0.4287
0.002	0.02	0.212	0.4604	0.2188	0.3576	0.4167
0.001	0.01	0.106	0.3256	0.2295	0.3469	0.4060
0.0004	0.004	0.0424	0.2083	0.2420	0.3344	0.3935
0.0002	0.002	0.0212	0.1456	0.2495	0.3269	0.3860
0.0001	0.001	0.0106	0.1029	0.2555	0.3209	0.3800
0.00004	0.0004	0.00424	0.0651	0.2615	0.3149	0.3740

In addition, the oxidation potentials were measured in mixtures containing ratios of potassium ferrocyanide and potassium ferricyanide of 10:1 and 1:10. The data are given in tables 2 and 3. They were recalcu-

TABLE 4

E.M.F. *measurements in 0.0004 molar ferrocyanide-ferricyanide mixture in the presence of salts*

SALT CONCENTRATION	TOTAL μ	SALT											
		KCl	$NaCl$	KNO_3	KBr	$NaC_2H_3O_2$	$NaNO_3$	$NaClO_4$	NH_4Cl	$LiCl$	$LiNO_3$	$RbCl$	$CsCl$
M													
0 5	0 5064	0 4581	0 4476	0 4560	0.4584		0 4482	0 4478	0.4588	0.4479	0 4482	0 4689	
0 25	0.2564	0 4422	0.4326	0.4416	0 4429		0 4334	0 4334	0.4428	0.4326	0.4324	0.4524	
0 10	0.1064	0 4244	0 4161	0 4242	0 4248	0 4154	0 4167	0 4164	0 4248	0.4161	0 4154	0.4334	
0 05	0 0564	0 4121	0.4054	0 4121	0 4124	0 4054	0 4059	0 4057	0.4123	0.4054	0.4046	0.4217	0.4324
0 025	0 0314	0.4014	0 3964	0 4014	0 4019	0 3957	0 3967	0.3964	0 4016	0.3964	0.3953	0 4079	0.4169
0.01	0 0164	0 3900	0 3872	0 3902	0 3906	0 3867	0.3874	0 3874	0 3902	0 3872	0.3869	0 3947	

TABLE 5

Influence of salts on the oxidation potential

CONCENTRATION OF SALT	TOTAL μ	SALT									
		K_2SO_4	Na_2SO_4	$Na_2C_2O_4$	$BaCl_2$	$Ba(NO_3)_2$	$SrCl_2$	$Ca(NO_3)_2$	$Mg(NO_3)_2$	Na_2CO_3	Na_2HPO_4
M											
0.1667	0.5064	0 4439	0.4354	0 4338	0 4717	0 4683	0 4684	0 4706	0 4762	0.4355	0.4354
0.0833	0 2564	0.4311	0 4231	0 4224	0 4588	0 4559	0 4557	0 4572	0 4614	0.4231	0.4231
0.0333	0.1064	0 4158	0 4090	0 4086	0 4444	0 4420	0 4414	0.4424	0 4454	0 4089	0.4090
0.0166	0 0564	0 4054	0 4000	0 3996	0 4342	0 4324	0 4314	0 4322	0 4347	0.4000	0.3998
0.00833	0.0314	0 3960	0.3920	0 3920	0 4237	0 4224	0 4209	0.4216	0.4237	0.3919	0.3920
0.00333	0.0164	0 3867	0 3844	0 3844	0.4009	0.4086	0 4076	0 4080	0 4094	0 3844	0.3844

lated on the basis of a ratio of the concentrations of 1:1 and correspond to the ϵ_0' values plotted in figure 2. These ϵ_0' values are identical with the values of the potential E measured in the equimolecular mixtures of ferrocyanide and ferricyanide. The reproducibility of the measurements in the very dilute solutions containing unequal molecular ratios of ferrocyanide and ferricyanide is not as good as of those reported in table 1; therefore, the extrapolated value of ϵ_0' at an ionic strength of zero is less reliable in the former cases.

The effect of neutral salts upon the potential

In all of the following determinations a solution containing 0.0004 molar potassium ferrocyanide and 0.0004 molar potassium ferricyanide, freshly prepared by dilution of a 0.01 molar mixture, was used. Ten ml. of the latter was diluted with conductivity water in a 250-ml. volumetric flask, a weighed amount of pure salt added, and the flask filled up to the mark. The results are given in tables 4, 5, and 6. "Total μ" refers to the sum of the ionic strengths of the added salt and of the 0.0004 molar ferrocyanide–ferricyanide mixture (μ = 0.0064). From equation 3 it is found that

TABLE 6

Influence of salts on the oxidation potential

TOTAL μ	CONCENTRATION OF $Na_4P_2O_7$	E (AGAINST NORMAL HYDROGEN ELECTRODE)	CONCENTRATION OF Na_3 CITRATE	E (AGAINST NORMAL HYDROGEN ELECTRODE)	CONCENTRATION OF $MgSO_4$	E (AGAINST NORMAL HYDROGEN ELECTRODE)
	M		*M*		*M*	
0.5064	0.05	0.4187	0.0833	0.4262	0.125	0.4584
0.2564	0.025	0.4097	0.0416	0.4154	0.0625	0.4474
0.1064	0.01	0.3987	0.0166	0.4034	0.025	0.4344
0.0564	0.005	0.3918	0.0083	0.3953	0.0125	0.4246
0.0314	0.025	0.3864	0.00416	0.3889	0.00625	0.4152
0.0164	0.001	0.3809	0.00166	0.3826	0.0025	0.4028

$$\log \frac{f_3}{f_4} = \frac{E - \epsilon_0}{0.0591}$$

The values of $\log f_3/f_4$ thus derived in various salt solutions are plotted in figure 3 against $\sqrt{\mu}$. The straight line again gives the values calculated with the assumption that the limiting Debye and Hückel expression holds at extreme dilutions.

DISCUSSION OF RESULTS

1. The generally accepted value of the normal potential of the ferro-ferricyanide electrode of 0.44 volt is much too high. At an ionic strength

of zero, a value of 0.356 volt was derived in this paper. From a practical viewpoint it is of interest to mention that the oxidation potential increases very rapidly with the increasing ionic strength and that it even can exceed the value of 0.44 in equimolecular mixtures of ferricyanide and ferrocyanide.

2. Even at infinite dilutions, the behavior of the system is not in harmony with the postulates of the simple Debye-Hückel expression. The slope of the curve giving the change of the oxidation potential or of log f_3/f_4 plotted against the square root of the ionic strength is greater than that calculated on the basis of the Debye-Hückel limiting equation. It is impossible to account for this anomaly on the basis of ionic size, using the present form of the Debye-Hückel theory, for, as V. K. La Mer (6) states, "absurd negative values of '*a*' would be demanded at very high dilutions followed by positive values in more concentrated solutions." Deviations of experimental data from the theoretically predicted curves have been described by various authors, a discussion of which is given in a paper by La Mer, Gronwall, and Greiff (7). Gronwall, La Mer, and Sandved (2) have shown that these discrepancies disappear if the influence of higher

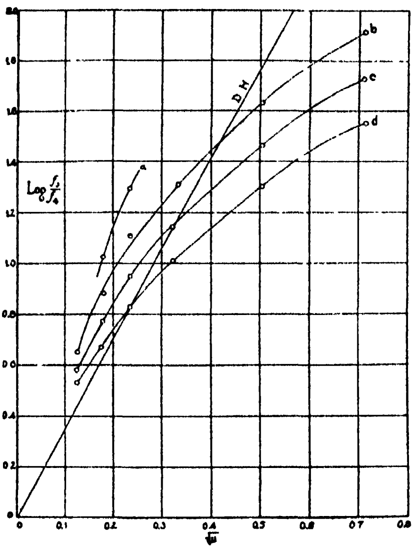

FIG. 3

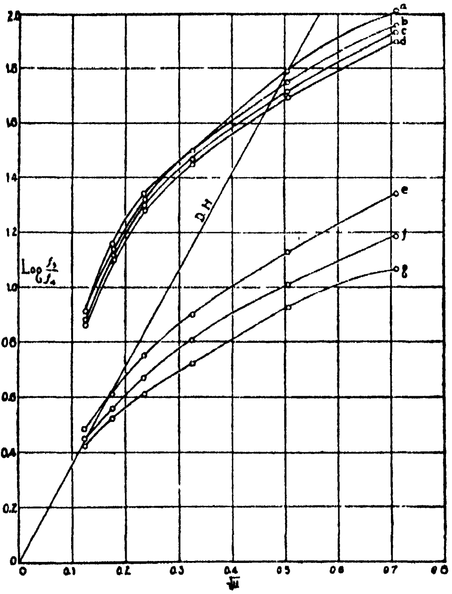

FIG. 4

FIG. 3.

a, CsCl; b, RbCl; c, KCl and NH_4Cl; d, LiCl. D. H., calculated from simple Debye-Hückel expression.

FIG. 4.

a, $Mg(NO_3)_2$; b, $BaCl_2$; c, $Ca(NO_3)_2$; d, $SrCl_2$; e, Na_2SO_4; f, Na_3 citrate; g, $Na_4P_2O_7$. D. H., calculated from simple Debye-Hückel expression.

terms of the Debye-Hückel theory in the case of unsymmetrical valence type electrolytes is taken into account. On the basis of the extended Debye-Hückel equation, values are found which fit the experimental data without assuming ion association or incomplete dissociation of the strong electrolytes. Undoubtedly, in a quantitative interpretation of the data found in this study, the extended equation of Gronwall, La Mer, and Sandved should be applied, since we are dealing with highly unsymmetric valence type electrolytes. Still, we have evidence to believe that even the extended equation does not account quantitatively for the results obtained, and that potassium ferrocyanide has to be considered as an incompletely dissociated electrolyte. In a subsequent paper, it will be shown that the curve obtained in a study of the potential of the potassium molybdo-molybdicyanide electrode, a system very similar to that of ferro–ferricyanide, does not intersect with the straight line calculated from the simple Debye-Hückel expression, but is found below this line even at extreme dilutions. In addition it was found that the fourth dissociation of molybdocyanic acid

$$HMo(CN)_8^{---} \rightarrow H^+ + Mo(CN)_8^{----}$$

is complete whereas that of ferrocyanic acid

$$HFe(CN)_6^{---} \rightleftarrows H^+ + Fe(CN)_6^{----}$$

is incomplete. This means that the proton combines with the ferrocyanide ion to form $HFe(CN)_6^{---}$, and it is quite plausible that other cations behave similarly. In the study of the influence of salts upon the potential of a very dilute potassium ferrocyanide–potassium ferricyanide mixture described in this paper it was found that the effect is virtually independent of the type of the anions. Potassium bromide, chloride, and nitrate have an identical effect at the same ionic strength; the same is true for sodium chloride, nitrate, and perchlorate on the one hand and sodium sulfate, oxalate, carbonate, and phosphate on the other.

The type of cation, however, has a very pronounced effect. With the alkali cations it decreased in the order Cs, Rb, K = NH_4, Na = Li, and we conclude that the degree of dissociation of the corresponding ferrocyanides decreased in the same order. The dissociation becomes more incomplete with the increasing valence of the cations, the effect of the various alkaline earths being of about the same order. This larger effect of the divalent ions is especially pronounced at the smaller ionic strengths.

Since the concentration of the cation is of primary importance, it is easily understood why the oxidation potentials found in potassium ferrocyanide–potassium ferricyanide mixtures of various ratios and recalculated on the basis of a ratio of 1:1 are not the same at the same ionic strength (figure 2). The potentials found increase from the mixture with a ratio of 10 ferrocyanide to 1 ferricyanide to that with a ratio of 1 to 10. In the former, the potassium–ion concentration is much smaller than in the latter at the same ionic strength. In a similar way, it is explained why the 1–2 valence types of electrolytes (sodium sulfate, carbonate, etc.) have a smaller effect than the 1–1 valence type of salts (sodium chloride, etc.).

SUMMARY

1. The normal potential of the ferrocyanide–ferricyanide electrode is equal to 0.3560 volt at 25°C.

2. The change of the potential of a very dilute ferrocyanide–ferricyanide solution with increasing ionic strength is greater than calculated on the basis of the simple Debye-Hückel expression. This is partly explained by incomplete dissociation of alkali and alkaline earth ferrocyanides.

3. For the same valence type of salts the anion effect upon the potential is the same for different anions at the same ionic strength. A pronounced cation effect was observed, the effect decreasing in the order Cs, Rb, K = NH_4, Na = Li for the alkali ions and being of about the same order for the alkaline earth ions. The latter, especially at the smaller ionic strengths, have a much greater effect than the univalent cations.

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THE FOURTH IONIZATION CONSTANT OF FERROCYANIC ACID[1]

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Strong acids increase the oxidation potential of a ferrocyanide–ferricyanide mixture much more than neutral salts at the same ionic strength. This effect was attributed by Kolthoff (1) to the pronounced basic properties of the ferrocyanide ion:

$$\mathrm{Fe(CN)_6^{----} + H^+ \rightleftharpoons HFe(CN)_6^{---}}$$

Since hydrogen ions remove ferrocyanide ions from the system they must increase the oxidation potential. From colorimetric measurements Kolthoff estimated the fourth ionization constant of ferrocyanic acid as being equal to 5 × 10^{-4}. He did not consider activities, and the value reported is very uncertain. In the present study the fourth ionization constant of ferrocyanic acid was derived from the effect of hydrogen ions upon the oxidation potential of a mixture of potassium ferrocyanide and potassium ferricyanide at known ionic strengths.

$$K_4 = \frac{a_{\mathrm{H^+}} \cdot a_{\mathrm{Fe(CN)_6^{----}}}}{a_{\mathrm{HFe(CN)_6^{---}}}} = \frac{a_{\mathrm{H^+}} \cdot c_{\mathrm{Fe(CN)_6^{----}}}}{c_{\mathrm{HFe(CN)_6}}} \cdot \frac{f_4}{f_3} \qquad (1)$$

$c_{\mathrm{Fe(CN)_6^{----}}}$ denotes the concentration of the ferrocyanide ions, $c_{\mathrm{HFe(CN)_6^{---}}}$ that of the hydroferrocyanide ions, and f_4/f_3 the ratio of their activity coefficients.

The oxidation potential of mixtures containing 0.0004 mole of potassium ferrocyanide and ferricyanide in a liter of a buffer solution of known paH was determined in the way described in the preceding paper (2). From the data reported before and the new measurements it was possible to evaluate K_4. It is assumed that the value of f_4/f_3 (equation 1) is the same as that of the activity coefficients of ferrocyanide and ferricyanide ions at the same ionic strength in the same electrolyte solution. Considering the similarity in structure and size of $\mathrm{Fe(CN)_6^{---}}$ and $\mathrm{HFe(CN)_6^{---}}$, the assumption of these trivalent ions having the same activity coefficients at the same ionic strength seems justified. The paH of the buffer solutions used was measured with a quinhydrone electrode using a similar electrode in a mixture of 0.01 *N* hydrochloric acid and 0.09 *N* potassium chloride as a standard half-cell. The paH of this mixture was taken to be equal to 2.075.

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[1] From the experimental part of a thesis submitted by William J. Tomsicek to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

The method of calculating the various data needed in solving equation 1 is demonstrated by the following example. The first measurement reported in table 1 gives an oxidation potential of 0.4156 volt against the normal hydrogen electrode in a mixture containing 0.0004 mole of potassium ferrocyanide and ferricyanide, 0.01 mole of sodium acetate, and 0.2 mole of acetic acid per liter. The paH of the buffer solution alone is 3.392, and the effect of the hydrogen ions upon the ionic strength is negligibly small. In table 4 of the previous paper (2) it was reported that the oxidation potential of an identical mixture without acetic acid was equal to 0.3867 volt. In each mixture the oxidation potential is given by the expression:

TABLE 1

Measurements in acetate buffers at 25°C.

CONCENTRATION OF ACETIC ACID	CONCENTRATION OF $NaC_2H_3O_2$	paH	$E_{\text{Q H.}}$	$E_{\text{N H.E.}}$	$K_4 \times 10^{-5}$
M	*M*				
0.2	0 01	3 392	0 1608	0 4156	5 8
0.1	0.01	3.683	0.1704	0.4060	5 6
0.05	0.01	3.983	0.1787	0 3977	5.7
Average					5 7

TABLE 2

Measurements in biphthalate–hydrochloric acid buffers

paH	$E_{\text{Q H.}}$	$E_{\text{N.H.E}}$	$K_4 \times 10^{-5}$
3.997	0.1607	0.4157	7.4
3.437	0.1500	0 4263	5.5
3 037	0.1363	0 4401	5 5
2.637	0.1163	0.4601	4 7
2.222	0.0893	0 4371	3.8
Average			5.4

TABLE 3

Measurements in dilute hydrochloric acid solutions

Molar concentration of HCl	0.0029	0.0058	0 0145	0.0291	0.0581
$E_{\text{N.H.E}}$	0.4577	0.4825	0.5173	0.5447	0.5735

TABLE 3

Osmotic pressure and ionic distribution data for solutions of crystallized horse serum albumin

NO.	SIDE OF MEMBRANE	TOTAL IN 320 CC OF SOLVENT (i + o) Cl	TOTAL IN 320 CC OF SOLVENT (i + o) Na	A	F	V	P_o	HYDROGEN-ION CONCENTRATION E M F	HYDROGEN-ION CONCENTRATION pH	HYDROGEN-ION CONCENTRATION $[H^+] \times 10^6$	E	R	$[Na^+] \times 10^6$	$[Cl^-] \times 10^6$	$W \times 10^6$	$\alpha' \times 10^6$	α'/W	$[T] \times 10^6$	$[D] \times 10^6$	P_c	$P_c - P_o$	$E\alpha' \times 10^4$	$A/V_i \times 25{,}280$	P_p $(M = 80{,}000)$	$P_c - P_o + P_p$	$\frac{E\alpha'}{P_c - P_o + P_p} \times 10^4$	$-\log \frac{E\alpha'}{P_c - P_o + P_p}$	$[+]_i \times 10^6$	$-\log [+]_i$
		eq $\times 10^3$	*eq.* $\times 10^3$	*gms*	*gms*	*cc.*	*cm* H_2O	*mv.*		*eq, l*	*mv*		*eq /l*	*eq /l*	*eq /g*	*eq /g*		*eq /l*	*eq /l*	*cm* H_2O	*cm* H_2O			*cm.* H_2O	*cm.* H_2O			*eq./l.*	
1	i	0 50	0	0.40	12 88	12 48	128 0	467 9	3 770	170	48 5	6 620	0	7425	383	227	0 590	7595	5350	135 2	7.2	109 8	810	10 1	17.3	6 35	3 197	170	3.770
	o					307 1		419 4	2 950	1122			0	1122				2244											
2	i	0 70	0 20	0 40	12 75	12 35	128 4	462 7	3 684	207	41 5	5 030	128	8510	440	253	0 575	8845	5461	138.0	9 6	104 7	819	10.2	19.8	5 29	3 277	335	3.475
	o					307 2		421 2	2 980	1047			644	1693				3384											
3	i	1 00	0.50	0 40	12 59	12 19	128 0	458 2	3 609	246	35 1	3 930	410	10140	499	289	0 580	10796	5636	142 5	14 5	101 4	829	10 3	24 8	4.09	3 388	656	3.183
	o					307 4		423 1	3 014	968			1610	2580				5160											
4	i	1 30	0 80	0 40	12 27	11 87	127 1	455 6	3 564	273	30 6	3 290	780	11410	548	307	0 560	12460	5520	139.5	12 4	94 1	852	10 6	23 0	4 09	3 388	1053	2.979
	o					307 7		425 0	3 045	902			2565	3470				6940											
5	i	1 50	1 00	0 40	11 62	11 22	127.7	454 3	3 542	287	28 5	3 030	1057	12330	570	308	0 540	13670	5530	139 8	12 1	87 8	901	11 2	23 3	37.7	3.424	1344	2 872
	o					308 4		425 8	3 060	871			3200	4070				8140											
6	i	1 80	1 30	0 40	11 17	10 77	127 8	453 1	3 521	301	26 0	2 750	1510	13700	603	320	0 530	15510	5550	140 3	12.5	83 2	939	11.7	24 2	3 44	3 463	1811	2.742
	o					308 9		427 1	3 082	828			4150	4980				9960											
7	i	2 50	2 00	0 40	9.94	9 54	127 4	449.5	3 462	345	21 7	2 328	2735	16780	616	327	0 530	19860	5500	139 0	11 6	71.0	1060	13.2	24 8	2 86	3.544	3080	2 511
	o					310 1		427 8	3 093	807			6370	7180				14360											
8	i	5 50	5 00	0 40	6 99	6 49	126 4	446 6	3 410	389	13 9	1 719	9190	28300	723	304	0 420	37880	4960	125.4	−1.0	42 2	1558	19.4	18 4	2 29	3.639	9580	2.019
	o					313 0		432 7	3 176	666			15790	16460				32920											
9	i	8.50	8.00	0 40	5.69	5 29	126 2	446 2	3 405	394	10.9	1 528	16480	39420	773	298	0 385	56290	4690	118 6	−7.6	32 5	1910	23.9	17.2	1.89	3.723	16874	1.773
	o					314 3		435 3	3 221	601			25200	25800				51600											
10	i	10.50	10.00	0 40	5 33	4 93	126 0	447 0	3 416	384	9 8	1 465	21460	46920	804	309	0.384	68760	4700	118.8	−7.2	30 3	2050	25 6	18.4	1.65	3.783	21844	1.660
	o					314.7		437 2	3 251	561			31470	32030				64060											

TABLE 2

Osmotic pressure and ionic distribution data for solutions of cow serum albumin

No.	Side of membrane	Total in 250 cc. of solvent (i + o): Cl × 10³ eq.	Total in 250 cc. of solvent (i + o): Na × 10³ eq.	A gms.	R gms.	V cc.	P° cm. H₂O	Hydrogen-ion concentration: E.M.F. mv.	Hydrogen-ion concentration: pH	Hydrogen-ion concentration: [H⁺] × 10⁶ eq./l.	E mv.	R	[Na⁺] × 10⁶ eq./l.	Chloride-ion concentration: E.M.F. mv.	Chloride-ion concentration: [Cl⁻] × 10⁶ eq./l.	W × 10⁶ eq./g.	α′ × 10⁶ eq./g.	α′/W	[T] × 10⁶ eq./l.	[D] × 10⁶ eq./l.	P^c cm. H₂O	$P^c - P^o$ cm. H₂O	$R\alpha' \times 10^4$	$A/V_i \times 25{,}380$	P^b (M = 60,000) cm. H₂O	$P^c - P^o + P^b$ cm. H₂O	$\frac{P^c - P^o + P^b}{R\alpha'} \times 10^4$	$-\log \frac{P^c - P^o + P^b}{R\alpha'}$	$[+]_i \times 10^6$ eq./l.	$-\log [+]_i$
1	o	0.50	0	0.40		308.6	128.2	418.5	2.935	1162	45.7	5.930	0	153.0	1175	348	186	0.535	2337	4830	122.0	−6.2	85.2	917	15.3	9.1	9.37	3.028	195	3.710
	i				11.43	11.03		464.2	3.710	195			0		6970				7165											
2	o	0.70	0.20	0.40		308.5	128.3	419.2	2.948	1127	39.6	4.680	641	143.2	1745	373	215	0.577	3515	5035	127.2	−1.1	85.4	913	15.2	14.1	6.05	3.218	378	3.422
	i				11.47	11.07		428.8	3.618	241			137		8170				8550											
3	o	1.00	0.50	0.40		308.7	127.6	421.1	2.980	1047	33.6	3.702	1604	132.6	2660	435	248	0.573	5310	5255	132.8	+5.2	83.6	923	15.4	20.6	4.06	3.392	717	3.144
	i				11.40	11.00		424.7	3.547	284			433		9850				10565											
4	o	1.30	0.80	0.40		309.3	127.9	422.1	2.997	1007	30.4	3.270	2560	125.2	3530	463	271	0.585	7100	5540	140.0	12.1	83.4	977	16.3	28.4	2.90	3.537	1090	2.963
	i				10.74	10.34		425.5	3.512	307			783		11550				12640											
5	o	1.50	1.00	0.40		309.1	127.2	423.2	3.012	973	28.7	3.060	3200	121.8	4145	497	276	0.555	8310	5730	144.8	17.6	79.2	1037	17.3	34.9	2.27	3.644	1363	2.866
	i				10.25	9.75		451.6	3.500	316			1047		12680				14040											
6	o	2.50	2.00	0.40		310.8	127.5	426.0	3.062	867	22.6	2.410	6360	108.0	7175	569	313	0.550	14400	5900	149.1	21.6	70.7	1155	19.5	41.1	1.72	3.764	2998	2.523
	i				9.15	8.75		448.6	3.446	358			2640		17300				20300											
7	o	5.50	5.00	0.40		313.0	126.6	430.8	3.128	744	15.4	1.820	15800	87.6	16670	661	351	0.531	33210	6230	157.2	30.6	54.1	1530	25.5	56.1	0.964	4.016	9101	2.041
	i				7.00	6.60		445.2	3.386	411			8690		30340				39440											
8	o	8.50	8.00	0.40		314.1	126.4	432.2	3.168	679	12.7	1.640	25200	76.6	26000	711	370	0.521	51880	6560	165.6	39.2	47.0	1833	30.9	70.1	0.670	4.174	15786	1.802
	i				5.91	5.51		444.6	3.381	416			15370		42650				58440											
9	o	10.50	10.00	0.40		314.7	126.6	433.2	3.183	656	11.6	1.571	31480	72.0	32340	729	370	0.507	64480	6770	170.8	44.2	43.0	2073	34.5	78.7	0.546	4.263	20446	1.689
	i				5.28	4.88		444.8	3.381	416			20030		50800				71250											
10	o	20.50	20.00	0.40		316.2	126.4	432.4	3.222	600	9.0	1.420	62780	56.0	63100	771	385	0.500	126480	7750	195.8	69.4	34.7	2948	49.1	118.5	0.293	4.533	44630	1.350
	i				3.83	3.43		444.4	3.373	424			44210		89600				134230											
11	o	50.50	50.00	0.40		318.3	124.7	436.1	3.284	520	Inside solution formed stiff gel																			
	i				1.78	1.38																								

TABLE 1

Osmotic pressure and ionic distribution data for solutions of crystallized egg albumin

NO.	SIDE OF MEMBRANE	TOTAL IN 320 cc. OF SOLVENT (i + o)		A	F	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^6$	$[Cl^-] \times 10^6$	$W \times 10^6$	$\alpha' \times 10^6$	α'/W	$[T] \times 10^6$	$[D] \times 10^6$	P_c	$P_c - P_o$	$E\alpha' \times 10^4$	$A/V_i \times 25{,}280$	P_p (M = 35,000)	$P_c - P_o + P_p$	$\frac{E\alpha'}{P_c - P_o + P_p} \times 10^4$	$-\log \frac{E\alpha'}{P_c - P_o + P_p}$	$[+]_i \times 10^6$	$-\log [+]_i$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^6$																			
		eq. $\times 10^3$	*eq* $\times 10^3$	*gms.*	*gms*	*cc.*	*cm* H_2O	*mv.*		*eq /l*	*mv*		*eq /l*	*eq /l.*	*eq /g.*	*eq./g*		*eq /l.*	*eq /l*	*cm.* H_2O	*cm* H_2O			*cm* H_2O	*cm* H_2O			*eq./l.*	
1	i	0.75	0	0.60	17.16	16.56	129.0	449.4	3.460	347	40.2	4.790	0	7980	399	211	0.529	8327	4993	126.2	−2.8	84.8	916	26.1	23.3	3.64	3.439	347	3.460
	o					302.8		409.2	2.778	1667			0	1667				3334											
2	i	0.95	0.20	0.60	16.00	15.40	128.9	444.9	3.382	415	35.5	3.980	163	9170	402	220	0.547	9748	5141	129.9	+1.0	78.2	984	28.1	29.1	2.69	3.571	578	3.238
	o					304.0		409.4	2.782	1652			650	2305				4607											
3	i	1.25	0.50	0.60	15.19	14.59	128.3	440.0	3.300	501	30.5	3.280	492	10700	401	236	0.588	11690	5170	130.6	2.3	72.0	1038	29.7	32.0	2.25	3.648	993	3.003
	o					304.8		409.5	2.783	1648			1615	3260				6520											
4	i	1.55	0.80	0.60	14.20	13.60	128.4	437.4	3.254	557	27.6	2.930	879	12325	396	247	0.623	13760	5350	135.1	6.7	68.2	1114	31.8	38.5	1.770	3.752	1436	2.842
	o					305.5		409.8	2.788	1630			2575	4205				8410											
5	i	1.75	1.00	0.60	13.96	13.36	128.2	436.2	3.236	581	26.3	2.786	1155	13480	410	261	0.638	15215	5539	140.0	11.8	68.8	1135	32.5	44.3	1.554	3.809	1736	2.760
	o					306.0		409.9	2.790	1621			3217	4838				9676											
6	i	2.75	2.00	0.60	11.91	11.31	128.0	432.8	3.179	662	21.3	2.292	2780	18070	454	276	0.603	21510	5740	145.0	17.0	58.8	1345	38.4	55.4	1.050	3.978	3440	2.463
	o					308.1		411.5	2.820	1514			6370	7884				15770											
7	i	5.75	5.00	0.60	8.95	8.35	127.2	428.0	3.096	801	14.5	1.761	9000	30400	507	286	0.565	40200	5700	144.0	16.8	41.5	1816	51.9	68.7	0.604	4.219	9800	2.009
	o					311.1		413.5	2.850	1412			15840	17250				34500											
8	i	10.75	10.00	0.60	7.18	6.58	126.7	426.1	3.064	862	10.7	1.516	20800	49800	556	309	0.556	71420	5780	146.0	19.3	33.1	2305	65.8	85.1	0.390	4.410	21660	1.664
	o					312.9		415.4	2.882	1312			31520	32830				65640											
9	i	30.75	30.00	0.60	Coagulated		125.0																						
	o																												

Legend for the tables: i and o signify inside and outside the membrane. Cl, Na = equivalents (total) of each of these atoms present in system (i + o). A = weight (in grams) of dry isoelectric protein present inside the membrane. F = weight (in grams) of the protein-containing solution (inside) at equilibrium. V = volume (in cc.) of solvent present at equilibrium (i and o). P_o = constant pressure (cm H_2O) (on inside solution) at which equilibrium was attained. $[H^+]$, $[Na^+]$, $[Cl^-]$ = concentrations (equivalents per liter) observed or calculated for these ions at equilibrium. $E = 59.1 \times (pH_i - pH_o)$ (in millivolts). R = antilog $E/59.1$ = ratio of distribution, $[H^+]_o/[H^+]_i$, of hydrogen ions at equilibrium. W = amount (equivalents) of hydrochloric acid which has combined with unit weight of protein (at equilibrium). α' = amount (equivalents) of chloride ion derived from unit weight of protein (chloride). α'/W = per cent dissociation of protein chloride. $[T]$ = total amount (equivalents per liter) of diffusible ions in the i and o solutions at equilibrium. $[D]$ = difference in amount (equivalents per liter) of diffusible ions inside and outside the membrane at equilibrium. $P_c = [D] \times 25280$ = calculated osmotic pressure due to diffusible ions alone. P_p = calculated osmotic pressure due to protein when the molecular weight has the value of M. $[+]_i$ = concentration (equivalents per liter) of diffusible ions inside the membrane and bearing the same sign of charge as the protein, i.e., a measure of foreign salt concentration inside.

with gum arabic this requirement was satisfied after calculations were made similar to those given above, so that it would seem that the assumptions were justified. In the case of the proteins, however, such calculations consistently led to the result that $(Cl^-)_o > (Na^+)_o + (H^+)_o$, which was taken to indicate that the protein chloride formed when hydrochloric acid came in contact with the isoelectric protein could not be assumed to be completely ionized. Therefore, instead of calculating the chloride-ion concentrations by the above equations, it was necessary to measure them, as described, with the silver-silver chloride electrode. This was done in the case of cow serum albumin. It was found that $(Cl^-)_o$ obtained in this manner closely agreed with the sum of $[H^+]_o$, obtained by measurement, and $(Na^+)_o$, obtained by calculation. With the other two proteins, then, this relationship was assumed to hold and the $(Cl^-)_o$ was taken to be equal to $(H^+)_o + (Na^+)_o$ without actually making the measurement with the silver-silver chloride electrode. From the $(Cl^-)_o$ value the $(Cl^-)_i$ value was obtained from the equation $(Cl^-)_i = R \cdot (Cl^-)_o$. (Electrode measurements of (Cl^-) in the presence of the colloid were never quite satisfactory, for some reason not yet determined. The voltage readings so obtained would indicate chloride-ion concentrations higher than those known to be present.) It is to be noted that hydrogen-ion activities are added to sodium-ion concentration outside. This is, of course, not strictly correct but apparently causes no great error, owing to the fact that at low ionic strengths the hydrogen-ion activity is very nearly equal to its concentration, while at those ionic strengths at which there would be an appreciable deviation of hydrogen-ion activity from hydrogen-ion concentrations, the amount of hydrogen ion present, as compared to sodium ion, has become so low as to make such a deviation (never more than 8 per cent) of minor importance in the totals.

In the tables, then, are given the calculated or measured values of the concentration per liter of each of the diffusible ions on each side of the membrane. These are totaled in the column under T and the difference between inside and outside is given under D. One mole of solute dissolved in 1 liter of solvent at 25°C. would give rise to an osmotic pressure equal to 25,280 cm. of water. This value multiplied by the value D in each experiment would give the osmotic pressure which should be derived from the unequal distribution of diffusible ions across the membrane (assuming their osmotic activity to be equivalent to their concentrations). The value, α', is defined as the number of equivalents of ions derived from unit weight of the colloid and can be calculated from the equation

$$\alpha' = \frac{(Cl^-)_i - [(H^+)_i + (Na^+)_i]}{A/V_i \times 1000}$$

A quantity not needed for calculating the relationship being tested but which is of interest is W, the equivalents of chloride combined with unit the total salt concentration present was varied sufficiently to give the desired curve. The temperature was 25°C. In some cases the chloride-ion concentration was measured in the external solution by means of the silver–silver chloride electrode. The chloride-ion concentration (rather than activity) was arrived at as follows: Voltage readings for a silver–silver chloride electrode, plus a saturated calomel half-cell, were made for solutions of hydrochloric acid and potassium chloride of known concentrations. The chloride-ion concentrations of these solutions were plotted against the voltage readings for the cell, and when voltage readings were obtained similarly for the external solutions of the above experiments (containing only hydrogen, sodium, and chloride ions), these were placed on this curve and the corresponding chloride-ion concentration read off.

It has been assumed that, in the concentration range studied in these experiments, the concentration ratio of distribution across the membrane for the various diffusible monovalent ionic species present does not vary more than a few per cent from the activity ratio as obtained from hydrogen-ion measurements. The concentrations of sodium ions on the two sides of the membrane can then be calculated by the equations

$$(\mathrm{Na}^+)_i = \frac{\text{Total Na present (equivalents)}}{(R \cdot V_o/1000) + V_i/1000}$$

and

$$(\mathrm{Na}^+)_o = R \cdot (\mathrm{Na}^+)_i$$

where

$$R = \frac{[\mathrm{H}^+]_o}{[\mathrm{H}^+]_i}$$

and V_o and V_i are the equilibrium volumes of solvent in cubic centimeters on the outside and inside of the membrane, respectively. Similarly the chloride-ion concentration could be calculated by the equations

$$(\mathrm{Cl}^-)_o = \frac{\text{Total Cl present (equivalents)}}{(R \cdot V_i/1000) + V_o/1000}$$

and

$$(\mathrm{Cl}^-)_i = R \cdot (\mathrm{Cl}^-)_o$$

If the above assumptions can be safely made, the results of the calculations must satisfy the requirement of electrical neutrality on each side of the membrane. Inside, the concentration of colloidal ions is unknown, but outside the membrane, where only monovalent diffusible ions are present, it is necessary that $(\mathrm{Na}^+)_o + (\mathrm{H}^+)_o = (\mathrm{Cl}^-)_o$. In the experiments of the protein is used in calculating P_p, the osmotic pressure due to the protein. Here $[+]_i$ is a measure of the foreign salt concentration in the colloid-containing solution and will be equal to $[H^+]_i + [Na]_i$, since these are the only ions present, other than the protein, bearing this charge. The osmotic pressure due to the colloid, P_p, is assumed to be directly proportional to the molar concentration of the colloid.

EXPERIMENTAL

Crystalline ovalbumin was prepared by the method of Cole (4) and was recrystallized three times. Crystalline horse serum albumin was prepared and was not recrystallized. Serum albumin from cow serum was not obtained crystalline but was dissolved and reprecipitated. Each of these proteins was dialyzed against water saturated with toluene until nearly free of sulfate ion, and then electrodialyzed until entirely free of salt ions. From the cow serum albumin there was always a fairly large percentage of the protein which precipitated during electrodialysis. This was removed from the supernatant solution before the latter was dried. The two crystalline proteins gave no precipitate during electrodialysis, although the salt-free solution of horse serum had the appearance of a definitely colloidal solution (Tyndall cone, etc.) in contrast to the clear solutions of the egg and serum albumins. These proteins were dried at room temperature and solutions of them were prepared as needed.

The method used for measuring osmotic pressure was the same as that employed in the gum arabic experiments (3). Small collodion sacs (about 15-cc. capacity) were used for membranes. In order to prevent the proteins from passing through the membranes it was necessary to dry them for a longer time in air before placing them in water than had been necessary with gum arabic. This in itself indicated that the molecular dimensions of the proteins were smaller than were those of the gum arabic. Known amounts (*A* in the tables) of the salt-free, isoelectric protein, in solution, were placed in the collodion sacs and these were connected with a source of constant pressure (P_o) and placed in contact with an external solution containing known amounts of hydrochloric acid and sodium chloride. The total water content of the system was known. A few drops of toluene were added to the external solution to act as a preservative for the protein. Equilibrium was attained in forty-eight to sixty hours, after which time the contents of the membranes were weighed (*F*) and the hydrogen-ion activity of the inner and outer solutions was determined electrometrically by means of a hydrogen electrode. From these measurements were obtained *R*, the ratio of distribution of each ionic species across the membrane, and *E*, the electrical potential existing across the membrane. All experiments were made on the acid side of the isoelectric point of the proteins, and for each protein a series of experiments was made in which derived from the unequally distributed diffusible ions. Such an assumption, of course, cannot be made with such proteins as egg and serum albumin, whose molecular weight is known to be low enough to give an osmotic pressure which would be of the same order of magnitude as that derived from the unequal distribution of the diffusible ions alone. However, if it can be assumed that the relationships found to exist for gum arabic solutions will also define the fraction of the osmotic pressure derived from the diffusible ions in solutions of such proteins, it should be possible to apply this correction and arrive at a value for the molecular weights of the proteins in the dilute salt solutions and at pH values other than the isoelectric point of the proteins. Conversely, if the accepted values of molecular weights and osmotic activity of the proteins can be assumed to hold for regions of pH distant from the isoelectric points and in dilute solutions, it becomes possible to correct the observed values of osmotic pressure in such protein solutions for the pressure due to the colloid and find whether or not the relationships found to exist for the gum arabic solutions are of general application in defining the osmotic pressure resulting from the unequal distribution of diffusible ions.

Where only monovalent diffusible ions are present, the empirical relationship found to exist in the experiments with gum arabic is given by the equation

$$\frac{E\alpha'[-]_i^{0.211}}{P_c - P_o} = \text{constant}$$

where P_o = the observed osmotic pressure at equilibrium, E = the membrane potential as obtained from electrometric hydrogen-ion measurements made upon the two solutions (inside and outside the membrane) after equilibrium had been reached, α' = the calculated equivalents of diffusible ions derived from unit weight of the colloid electrolyte, $[-]_i$ = the calculated concentration of diffusible ions of the same charge as that of the colloid present inside the membrane at equilibrium and is a measure of the foreign salt concentration in the solution containing the colloid, and P_c = the osmotic pressure to be expected from the difference in total diffusible ion concentrations across the membrane at equilibrium. When $\log \frac{E\alpha'}{P_c - P_o}$ is plotted against the $\log [-]_i$ a straight line is obtained with a slope equal to 0.211. The slope of the curve is not the same for all colloids, but does not show any lyotropic effect between ions of equal valence (i.e., H^+, Na^+, Li^+, etc.).

Since the proteins on the acid side of their isoelectric points are positively charged colloids, it should be possible to obtain a straight line when the $\log \frac{E\alpha'}{P_c - (P_o - P_p)}$ is plotted against $\log [+]_i$ if the correct molecular weight

APPLICATION OF AN EMPIRICAL CORRECTION TO THE DONNAN EFFECT IN THE ESTIMATION OF MOLECULAR WEIGHTS OF PROTEINS BY OSMOTIC PRESSURE MEASUREMENTS

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Osmotic pressure determinations of the molecular weights of proteins have hitherto been made at the isoelectric points, or within a pH range very close to the isoelectric points, of the proteins, and in the presence of high concentrations of salts. This procedure has been necessary in order to eliminate the osmotic effects of ions other than the colloid, resulting from the setting up of a Donnan equilibrium in which there exists an unequal distribution of diffusible ions on the two sides of the membrane. According to the Donnan theory of membrane equilibria, a knowledge of the active concentrations of these diffusible ions in the inner, colloid-containing solution, and in the outer solution with which it is in equilibrium, would make possible the estimation of the fraction of the observed osmotic pressure due to these ions, which, when corrected for, would give the osmotic pressure due to the colloid even at points distant from the isoelectric point and in dilute solutions. Attempts to make such corrections have repeatedly been unsatisfactory, however, and the results have been taken to indicate, among other things, variations in size of molecule of the colloid (2, 5), change in the osmotic activity of the colloidal molecule (1), and absence of, or modified osmotic activity of the diffusible ions derived from the colloid electrolyte (Gegenionen) (6, 7, 8).

In a series of experiments (3) in which the osmotic pressure of purified gum arabic was studied throughout a range of variation in the concentration of colloid, pH, and concentration of foreign salt, an empirical relationship has been found to exist between certain determinable variables in the system and the deviation of the observed osmotic pressure from that calculated upon the basis of differences in concentration of the diffusible ions across the membrane at equilibrium. This relationship was arrived at by assuming that the colloid micelle itself showed no appreciable osmotic pressure, in that the molecular weight of the arabate ion was so high that osmotic pressure due to the micelle was negligible in comparison with that

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evaluating σ_0, but does not prevent their being used to decide whether an anomaly exists in connection with variations in length at constant radius.

Essentially similar results were obtained in some preliminary tests with soils, but for the reasons already stated, we have given the details of the experiments only in the case of barium sulfate.

CONCLUSIONS

These measurements show quite conclusively that for barium sulfate paste the rate of flow in tubes of a given radius and under a given pressure gradient (within the limits used) is independent of the length of the tube. The data thus lend no support to the idea that this material suffers a progressive breakdown with time under shear.

The effect of changing the radius upon the position of the $V/\pi R^3$–$PR/2L$ curves is as marked as in the earlier experiments on this material. From a calculation made from the curves published in an earlier paper (7), it may be concluded that the thickness of the layer which is modified by its proximity to the wall of the tube cannot be less than 20μ (the thickness, if this layer had the viscosity of pure water). This is very remarkable, since we now know that the individual particles are only 2 to 3μ in linear diameter. The thickness of the modified layer seems to be more comparable with the size of the flocculated aggregates as shown by sedimentation.

SUMMARY

Measurements have been made of the rate of flow of an aqueous paste of barium sulfate through tubes differing considerably both in radius and length under a series of pressure heads. The results show that for tubes of the same radius and under the same pressure gradient, the rate of flow is independent of the length of the tube; from which it is concluded that under the conditions of these experiments, this material shows no progressive breakdown with time under shear, as suggested by Ambrose and Loomis (1) for bentonite.

For different radii, however, curves for $V/\pi R^3$ against $PR/2L$ were obtained which, as previously recorded, do not coincide as they should if at every point in the tube the velocity gradient depends only on the shearing stress.

The hypothesis previously advanced that the proximity of the wall of the tube causes a sheath of material to shear more easily than does the bulk of the material, appears therefore to be the only one so far advanced that accounts for the facts.

The case of this barium sulfate paste is particularly interesting, as the particles are roughly cubical in form, and the thickness of the modified layer is many times the average particle diameter.

resistance, end-effect corrections were neglected. (Cv. Ambrose and Loomis' criticisms of capillary tube methods.)

Table 2 gives the results of experiment A, and table 3 of experiment B. The data are also plotted in figures 1 and 2, plotting $V/100\pi R^3$ against $\frac{W}{100}$, where $W = PR\Delta g/2L$. V is flow in cubic centimeters per second and equals flowmeter reading "a" × appropriate constant. P is pressure (cm. Hg) corrected for bulb resistance, and P_m the uncorrected pressure as read on the manometer.

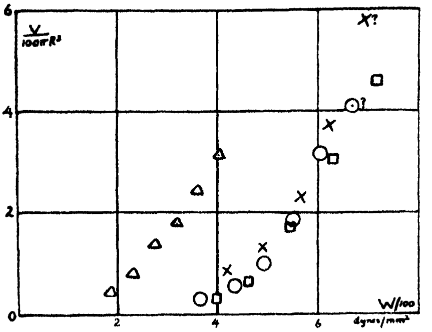

FIG. 1

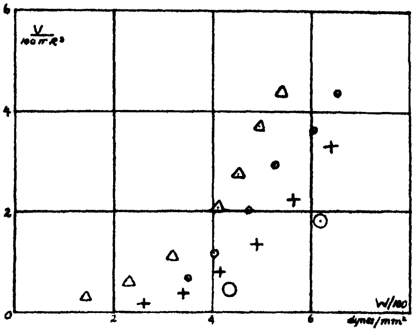

FIG. 2

FIG. 1

⊙ Capillary a, R = 0.126 cm., L = 11.8 cm.
△ Capillary V, R = 0.0407 cm., L = 12.3 cm.
× Capillary b, R = 0.129 cm., L = 22.5 cm.
⊡ Capillary j, R = 0.126 cm., L = 7.5 cm.

FIG. 2

⊙ Capillary a, R = 0.126 cm., L = 11.8 cm.
△ Capillary V, R = 0.0407 cm., L = 12.3 cm.
+ Capillary III, R = 0.073 cm., L = 12.1 cm.
○ Capillary IV, R = 0.048 cm., L = 12.25 cm.

The figures in the second column of each table refer to the resistance used in the flowmeter. For (2) flowmeter readings (a) are multiplied by 0.277. For (6) flowmeter readings (a) are multiplied by 0.029.

Figure 1 shows that length of tube has no effect on consistency, within the limits investigated, whereas the tube having a different radius shows an entirely different curve. The σ-effect (effect of radius) is shown more definitely in experiment B (figure 2).

The maximum length of tube used was 40 cm., as compared with 10 cm. in the earlier experiments, and with the apparatus in its present form stage IV could only be reached at the highest pressures. Most of the points therefore, are in stage III. This makes the data unsuitable for tions of very soluble salts, but that no such errors occur in the case of pastes of soils or clays. There is no reason to suspect any such trouble with pastes of insoluble barium sulfate, and in any case the effect would be small compared with the very gross phenomena being investigated in these experiments. A series of tubes having the dimensions shown in table 1(a), was prepared. The radii were determined by a viscometric comparison with our previously carefully standardized tubes (table 1(b)) by measuring the flow/stress ratio for a glycerol–water solution for each tube, and so calculating R. Corrections for resistance in plastometer bulbs were made throughout by connecting the bulbs directly together as described in the first paper of this series (7).

TABLE 3

Results of experiment B

CAPILLARY	RESISTANCE USED IN FLOWMETER	P_m	a	V	P	$W/100$	$V/100\,\pi R^3$
V	(6)	8.0	0.2	0.006	6.5	1.43	0.280
		12.0	0.4	0.012	10.5	2.30	0.569
		16.0	0.8	0.023	14.5	3.18	1.09
		20.0	1.5	0.044	18.5	4.07	2.07
		22.0	2.0	0.058	20.4	4.50	2.75
		24.0	2.7	0.078	22.4	4.92	3.70
		26.0	3.2	0.093	24.4	5.39	4.40
III	(6)	8.0	0.7	0.020	6.5	2.60	0.165
		10.0	1.5	0.044	8.5	3.40	0.365
		12.0	3.3	0.096	10.4	4.15	0.795
		14.0	5.6	0.162	12.2	4.88	1.34
		16.0	9.2	0.267	14.1	5.62	2.22
		18.0	13.8	0.400	16.0	6.40	3.30
IV	(6)	15.0	0.8	0.023	13.5	3.50	0.665
		17.0	1.4	0.041	15.3	4.03	1.19
		20.0	2.4	0.070	18.4	4.73	2.04
		22.0	3.5	0.102	20.3	5.25	2.95
		25.0	4.3	0.125	23.2	6.02	3.62
		27.0	5.2	0.151	25.2	6.55	4.38
a (incomplete)	(2)	8.0	1.0	0.277	6.15	4.33	0.448
		11.0	4.0	1.11	8.8	6.18	1.80

Tube h showed slightly anomalous behavior, but, since its L/R ratio is only 36, this was disregarded.

Since the presence of a small metal disk drilled with a hole of 0.14 cm. radius in place of a capillary made no serious difference to the plastometer

Preliminary measurements made without the use of vaseline gave essentially similar results, but the accuracy was less, owing to the difficulty of observing the level of the material in the bulbs.

Moreover, slight losses of material during the changing of the tubes and the advisability of continuing a given experiment over too long a period of time also precluded the use of a very great number of tubes for each experiment, and introduced an element of haste into the experiments which prevented their accuracy from equalling that of the earlier and more leisurely experiments. They were, nevertheless, amply accurate for the purpose in hand.

TABLE 2

Results of experiment A

Capillaries are given in the order in which the experiments were done

CAPILLARY	RESISTANCE USED IN FLOW-METER	P_m	a	V	P	$W/100$	$V/100\,\pi R^3$
a	(2)	7.0	0.6	0.167	5.2	3.65	0.266
		8.0	1.2	0.333	6.15	4.35	0.535
		9.0	2.2	0.61	7.0	4.94	0.985
		10.0	4.1	1.14	7.8	5.50	1.84
		11.0	7.1	1.97	8.6	6.05	3.18
		12.0	9.1 (?)	2.52 (?)	9.5	6.70	4.07 (?)
b	(2)	13.0	2.0	0.555	11.0	4.17	0.825
		15.0	3.1	0.86	12.9	4.90	1.28
		17.0	5.5	1.53	14.85	5.65	2.27
		19.0	9.0	2.50	16.5	6.25	3.72
		21.0	14.0 (?)	3.90 (?)	18.3	6.95	5.80 (?)
j	(2)	5.0	0.6	0.167	3.2	3.59	0.265
		6.0	1.4	0.388	4.1	4.6	0.619
		7.0	3.9	1.08	4.85	5.45	1.71
		8.0	6.9	1.91	5.6	6.3	3.02
		9.0	10.5	2.90	6.4	7.2	4.60
V	(6)	10.0	0.3	0.009	8.4	1.85	0.425
		12.0	0.6	0.017	10.4	2.28	0.800
		14.0	1.0	0.029	12.4	2.72	1.38
		16.0	1.3	0.038	14.4	3.17	1.80
		18.0	1.8	0.052	16.3	3.59	2.45
		20.0	2.3	0.067	18.3	4.02	3.15

The plastometer bulbs were connected to the capillary by means of rubber sleeves. In earlier papers (14, 15) it was shown that such a procedure was liable to cause unexpected errors in the case of saturated soluquotes our work and suggests that ammonium oleate sols show a "plug flow." This is demonstrably not so in the sense in which we use the words, and in any case it seems more likely that the disturbance he observes is due to the elasticity of the sol than to anomalous flow.

EXPERIMENTAL PART

As already recorded, the phenomenon under consideration was first observed in pastes of soils and clays. The composition of these materials is, however, highly variable, and the extent of the phenomenon depends on factors not all of which are understood. Since the question at issue is a fundamental one, it seemed wisest to use, for the present tests, a material of simple and known composition which is easily procurable by others who may wish to repeat the experiments. Barium sulfate (pure) as supplied by British Drug Houses was therefore selected. Microscopic examination showed that the material was reasonably homogeneous and consisted mainly of cubes with sides 2 to 3μ in length.

TABLE 1

(a)			(b)		
TUBE NO	*R*	*L*	TUBE NO.	*R*	*L*
	cm.	*cm.*		*cm.*	*cm*
h	0.131	4.7	III	0.073	12 10
j	0 126	7 5	IV	0.048	12 25
a	0.126	11 8	V	0 0407	12 30
b	0 129	22 5			

In preparing this paste, the barium sulfate was triturated with distilled water with a rubber pestle, then gently pressed through a 100 mesh per inch sieve, thoroughly stirred, sieved again, bottled, brought to temperature (25°C.) in the thermostat, well shaken and then tested in the plastometer (A). Another portion of the same sample was kept overnight, and tested the next day (B). The concentration of the two samples differed slightly, but a moisture test at the end of the second experiment showed that 100 g. of paste had contained about 55 g. of dry barium sulfate.

Owing to the tendency for the barium sulfate paste not to leave a clean surface on the walls of the plastometer tubes, the insides of the bulbs were coated with a thin layer of vaseline. This worked excellently until the material had been sheared a considerable number of times, when small spots of the vaseline surface rubbed off, and got into the capillary, readings then becoming erratic. This happening was well defined, all readings up to a certain time being steady and reproducible, but this difficulty precluded a comparison of a very great number of tubes in a single experiment.

radius of the tube, or is the association indirect, the governing factor being in reality the proportions of the tube, i.e. the ratio of some function of the radius to the length?

GENERAL BEHAVIOR OF THE MATERIALS INVESTIGATED

Before giving detailed consideration to the new data, it will be as well to recapitulate very briefly the flow characteristics of the aqueous paste, which are fully set out in the paper already referred to. Four stages may be distinguished as the pressure gradient is increased from zero.

Stage I. No movement.

Stage II.[2] Slow movement as a solid plug, flow increasing linearly with pressure.

Stage III. A very rapid increase of flow with pressure, the plug being separated from the wall by a sheath of material in laminar flow.

Stage IV. Rapid flow increasing almost linearly with pressure, the central plug occupying only a small part of the cross section and having little influence.

According to the mathematical treatments of Buckingham (3) and Reiner (6) stage III is reached when the shearing stress W at the wall of the tube surpasses the critical shearing stress (S_0) of the material, and the sheath of material in laminar flow should have a thickness $R(W - S_0)/W$ which is proportional to the radius of the tube. The mean velocity of flow $V/\pi R^2$ for a given value of W greater than S_0 should therefore be proportional to R, which is another way of saying that the curve of $V/\pi R^3$ against W should be independent of R. The fact that the $V/\pi R^3$–W curve is not independent of R is interpreted by us as indicating that mean velocity of $V/\pi R^2$ may be resolved into two parts, one proportional to R, and the other independent of it. The part that is independent of R is mathematically similar to the term introduced by Buckingham to cover stage II. But whereas the velocity of sliding of the plug in stage II is so low that the lubricating sheath, assumed to consist of water, has a mean thickness of only 10^{-5} cm., the additional term needed to account for the flow in stages III and IV is about one hundred times as great.

In order to get a quantitative measure of the anomaly in stage IV, it was found convenient to plot the mean velocity $V/\pi R^2$ against W. The best straight lines making a common intercept on the W-axis were drawn, and their slopes σ plotted against R. The extent of the anomaly is indicated by the intercept σ_0 of this derived graph on the σ-axis; hence the name σ-phenomenon.

The need for a reiteration of the distinction between the "plug flow" of stage II and the anomalous flow near the wall of the tube which sometimes occurs in stages III and IV, is evident from a paper by Lawrence (4), who fied layer, in the case of a certain soil paste, it could not be greater than 8×10^{-3} cm. or less than 1×10^{-3} cm.

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[2] For work on stage II, see references 11, 12, and 16.

A different hypothesis has recently been put forward by Ambrose and Loomis (1) to account for the anomalous behavior of bentonite pastes. They point out that bentonite is known to be thixotropic, and suggest that the velocity gradient depends not only on the magnitude of the shearing stress, but also on the time it is applied. They conclude that this material appears to have a lower consistency the narrower the tube used, because "for constant shearing stress at the wall, the material flows at higher linear velocity in the larger tubes, thus being subjected to the same distribution of shearing stresses for a shorter time than in the smaller tubes."

While it is possible that, with the material used by these authors and under the conditions of their experiments, thixotropy may have been of importance, we do not think it can have had any measurable influence on our published data. Before any measurements were made, the whole of the material was driven through the tube from one bulb into the other, and although the direction of flow had to be reversed several times to get a complete set of points for a curve, the experimental figures give no indication that time of shear influences the rate of flow.[1] Feeling, nevertheless, that the matter should be further investigated, we have made new measurements on several of the materials studied before, using tubes which differ considerably in length as well as in radius. It is clear that, if the material flows more readily under a given stress the longer it is applied, the rate of extrusion under a given pressure gradient will increase with the length of a tube of given radius. Comparatively little work has been done on the effect of length of tube on consistency. Our own earlier experiments (13) were confined to a comparatively small difference of length. Ambrose and Loomis (1) quote Peek and Erickson (5) as having "learned that the apparent viscosity of agar solutions and starch pastes at constant shearing stress is lower in the longer tubes," though these authors themselves say that they "do not consider the data conclusive evidence of a difference of the type observed." On the contrary Staudinger and Heuer (17) state that "the solution of a high polymer (polystyrol) flowing through a long tube appears more viscous than in a short tube of the same diameter, since here, owing to the long fiber molecules, the hindrance to a normal flow is more marked" (our translation).

The point which we have set out to settle is, therefore, this: Is the variation of $V/\pi R^3$ for a given value of W, which we have observed in aqueous pastes of certain soils, clays, and minerals, directly associated with the

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[1] When materials showing marked thixotropy are investigated in our instrument, the flowmeter readings for a given pressure do not remain steady, but tend to increase so long as the shearing is continued. In consequence of this, we have not published any data for such materials.

THE INFLUENCE OF THE PROXIMITY OF A SOLID WALL ON THE CONSISTENCY OF VISCOUS AND PLASTIC MATERIALS. IV

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INTRODUCTION

In the first paper (7) of this series experiments were described in which aqueous pastes of soils, clays, and finely divided minerals were forced through narrow glass tubes. The instrument used was the modified Bingham plastometer described in an earlier paper (13), in which two bulbs are connected by a tube of known length L and radius R. The material can be made to flow in either direction under a measured air pressure P. The volume V of flow per second was measured indirectly by the small back-pressure set up by the air in escaping through one of a series of standardized capillary leaks.

The data so obtained presented a problem, for on plotting $V/\pi R^3$ against $PR/2L$ ($= W$, the shearing stress per unit area on the wall of the tube) the points for tubes of different radii did not fall on the same curve, those for a narrower tube lying above those for a wider one. It was already known from the work of Bingham (2) and others, that such materials do not conform to Poiseuille's law, which means that the velocity gradient is not directly proportional to the shearing stress as it is for true fluids; but it was shown that no equation of dependence of velocity gradient on shearing stress, however complicated, would account for the phenomenon. The discrepancy is far too large to be put down to experimental error, and the only possible conclusion is that somewhere in the tube the velocity gradient depends on *something else besides the shearing stress.* So much seems certain.

An examination of the data obtained with a series of different radii led us to put forward the hypothesis that the *proximity of a solid wall* is the disturbing factor. It was suggested that, where the $V/\pi R^3$-W curves for different radii were not coincident, a shearing stress operating near the wall of the tube gives rise to a greater velocity gradient than does the same stress operating in the bulk of the material. In the subsequent papers of this series (8, 10) it was shown that although the data are not sufficiently exact to enable a precise estimate to be made of the thickness of the modi-

one or two experimental points in regions where the percentage of water is high. It was found, however, that the experimental values of the refractive index at different alcohol ratios (table 2) when plotted on a large scale as in figure 2 enabled lines of constant refractive index to be drawn on the ternary as shown in figure 1. From the index of refraction of the equilibrium layers, the compositions of the solutions as indicated by the tie lines were correct to within ±0.2 per cent.

SUMMARY

The solubilities, densities, and indices of refraction have been determined for the system isoamyl alcohol–propyl alcohol–water at 25°C. Tie lines were determined for nine pairs of solutions.

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determined for a series of nine different mixtures having a total composition inside the solubility curve (i.e., the heterogeneous area). These compositions are shown in table 3. It was thought that the compositions of the equilibrium layers could be obtained by using the method of Smith (4), who investigated the system methyl alcohol–isobutyl alcohol–water.

TABLE 3

Composition of layers in equilibrium at 25°C.

UPPER LAYER				LOWER LAYER			
Index of refraction	Volume per cent isoamyl alcohol	Volume per cent *n*-propyl alcohol	Volume per cent water	Index of refraction	Volume per cent isoamyl alcohol	Volume per cent *n*-propyl alcohol	Volume per cent water
1.3987	81.8	8.7	9.5	1.3375	2.6	3.9	93.5
1.3965	74.1	15.2	10.7	1.3383	2.8	5.0	92.2
1.3943	65.8	22.2	12.0	1.3404	2.8	7.8	89.4
1.3921	57.9	28.1	14.0	1.3422	3.0	10.0	87.0
1.3903	52.1	32.9	15.0	1.3434	2.7	12.3	85.0
1.3871	41.9	39.6	18.5	1.3449	2.5	14.5	83.0
1.3851	37.5	42.0	20.5	1.3461	2.9	16.2	80.9
1.3828	31.3	45.0	23.7	1.3480	3.0	20.8	76.2
1.3802	25.1	46.8	28.1	1.3506	3.0	22.2	74.8

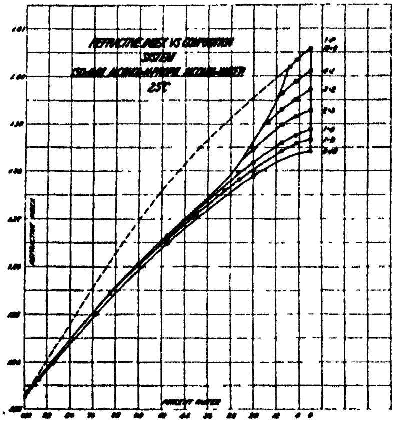

FIG. 2. REFRACTIVE INDEX VERSUS COMPOSITION FOR THE SYSTEM ISOAMYL ALCOHOL–*n*-PROPYL ALCOHOL–WATER AT 25°C.

Because of the relatively large portion of the ternary diagram over which the liquids are insoluble, as compared with the system investigated by Smith, it becomes a matter of the utmost difficulty to draw the lines for refractive index vs. alcohol ratio, at constant water content. This difficulty arises from the fact that large extrapolations have to be made from

TABLE 2

Values of the refractive index at different alcohol ratios

ALCOHOL RATIO I/P	VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT *n*-PROPYL ALCOHOL	VOLUME PER CENT WATER	REFRACTIVE INDEX AT 25°C.	SPECIFIC GRAVITY AT 25°C.
0/10		100.0		1.3841	0.8016
		80.0	20.0	1.3788	0.8527
		50.0	50.0	1.3648	0.9163
		25.0	75.0	1.3501	0.9652
		10.0	90.0	1.3398	0.9852
		5.0	95.0	1.3368	0.9911
1/9	9.6	85.4	5.0	1.3859	0.8158
	9.1	80.9	10.0	1.3842	0.8286
	8.1	71.9	20.0	1.3800	0.8522
	7.8	67.2	25.0	1.3781	0.8634
	7.1	62.9	30.0	1.3760	0.8742
	6.1	53.9	40.0	1.3709	0.8955
	5.1	44.9	50.0	1.3655	0.9164
	4.2	35.8	60.0	1.3607	0.9359
	3.1	26.9	70.0	1.3545	0.9548
	10.0	90.0		1.3867	0.8025
2/8	20.0	80.0		1.3888	0.8028
	19.2	75.8	5.0	1.3875	0.8159
	18.2	71.8	10.0	1.3860	0.8286
	16.2	63.8	20.0	1.3817	0.8154
	15.1	59.9	25.0	1.3797	0.8633
	14.2	55.8	30.0	1.3771	0.8741
	12.2	47.8	40.0	1.3719	0.8948
2/3	40.0	60.0		1.3929	0.8043
	38.0	57.0	5.0	1.3915	0.8166
	36.0	54.0	10.0	1.3898	0.8293
	32.0	48.0	20.0	1.3846	0.8156
3/2	60.0	40.0		1.3973	0.8051
	57.0	38.0	5.0	1.3952	0.8181
	54.0	36.0	10.0	1.3930	0.8291
	51.0	34.0	15.0	1.3904	0.8402
8/2	80.0	20.0		1.4011	0.8082
	76.0	19.0	5.0	1.3988	0.8174
	72.0	18.0	10.0	1.3964	0.8291
10/0	100.0			1.4058	0.8061
	95.0		5.0	1.4033	0.8177
	93.0		7.0	1.4018	0.8220
	2.0		98.0	1.3346	0.9949

Certain portions of the curve were determined by using mixtures of water and propyl alcohol, to which isoamyl alcohol was added. These results are shown in table 1. The densities were determined in the usual manner, care being taken to keep the solutions at 25°C. In making the index of refraction measurements, trouble was experienced in getting a suitable cement on which the isoamyl alcohol had little solvent action. Picene was unsatisfactory for this reason. Fish glue could not be used because of its solubility in water. If, however, the cleaned surfaces were treated with a thin layer of Canada balsam and were allowed to stand from two to three days, no trouble was experienced.

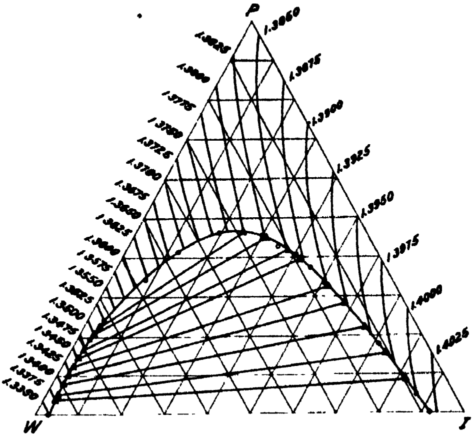

FIG. 1. THE SOLUBILITY CURVE

TABLE 1

Solubility of isoamyl and propyl alcohols in water at 25°C.

VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT *n*-PROPYL ALCOHOL	VOLUME PER CENT WATER	VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT *n*-PROPYL ALCOHOL	VOLUME PER CENT WATER
40.40	40.40	19.20	19.80	46.21	33.99
45.47	37.21	17.32	13.77	41.32	44.91
50.63	33.76	15.61	8.60	34.40	57.00
60.84	26.08	13.08	2.53	19.50	77.97
71.10	17.78	11.12	4.08	23.98	71.94
81.37	9.04	9.59	2.44	4.88	92.68
86.83	4.57	8.60	2.29	9.77	87.94
89.90	2.30	9.22	2.25	14.66	83.09
93.32		6.68	2.53	19.49	77.98
35.02	42.81	22.17	4.03	23.99	71.98
30.17	45.26	24.57	3.10		96.90
25.10	46.59	28.31			

In addition to the solubility curve, equilibrium compositions were

THE TERNARY SYSTEM ISOAMYL ALCOHOL–PROPYL ALCOHOL–WATER

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INTRODUCTION

In the course of investigating the solubilities of the alkali chlorides in mixtures of isoamyl alcohol, propyl alcohol, and water, it was found necessary to determine the limits of the solubility of these three liquids. Although a large number of alcohol–water systems have been investigated, we were unable to find solubility data for the above system.

MATERIALS

The isoamyl alcohol was Baker's A.C.S. reagent grade, which boiled over a range of 128–132.5°C. and was therefore subjected to fractional distillation, the fraction coming over at a constant boiling point of 130.5°C. being collected. This agrees with the accepted value (2). The normal propyl alcohol was redistilled and the fraction boiling at 97.8 ±0.1°C. was taken (3).

APPARATUS

A Zeiss Pulfrich refractometer was used in determining the indices of refraction. The values could be read to 0.00005 and were rounded off to the nearest 0.0001. The temperature of the liquid in the prism cup was held at 25 ±0.1°C. by means of a circulating stream of water as described by Hoyt (1). The Westphal balance used in the density determinations was checked against a 25-cc. pyknometer. It was found that using a 10-cc. float the error involved was ±0.0001. The solutions were prepared by mixing known volumes of the three liquids at 25°C., and were correct to ±0.1 per cent.

PROCEDURE AND DISCUSSION

The solubility curve, figure 1, was determined by placing a series of constant isoamyl–propyl alcohol mixtures, each of 200 cc., in a thermostat at 25 ±0.01°C. Each sample was thoroughly agitated while water was being added until the first appearance of turbidity was noted. The agitation was continued over a period of six to eight hours to ensure equilibrium.

The writer wishes to thank Dr. T. R. Hogness for the helpful discussions regarding this paper.

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along the line SS_2. The arbitrariness of this type of procedure made the author feel that this as well as other limitations of the proposed arrangement[3] could best be appreciated after an experimental attempt has been made. It is to be noted that this type of condenser valve is inherent in the apparatus of Smythe and Mattauch and thus has been proved quite successful. Hence, its effects on the width of the mass and velocity peaks as well as those due to the bending of the lines of force at the entrance of the analyzing field, the influence of other perturbing fields, etc., can be calculated in a general way similar to the one used by Herzog and Mattauch, to which the reader is referred.

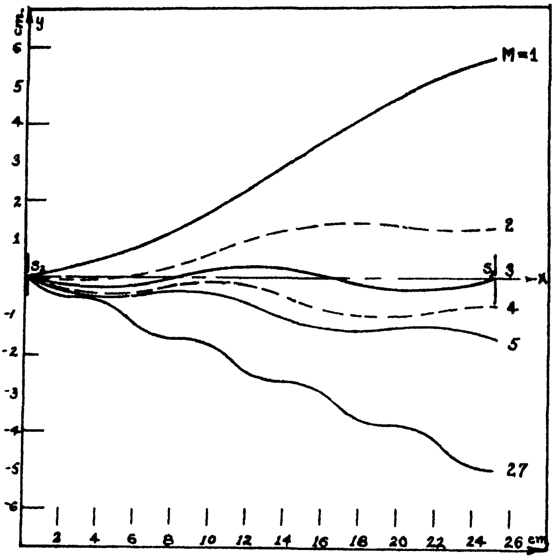

FIG. 4. CONDITIONS CHOSEN SO THAT IONS WITH $M = 3$ FOCUS ON RECEIVING SLIT

The study of the trajectories of the ions in this type of apparatus is instructive. Under the conditions given below, the curves in figure 4 were traced for the masses 1, 2, 3, 4, 5, and 27, using the expression

$$y = \frac{e}{m}\frac{a_1}{2\pi f}\left(\sqrt{\frac{m}{2eV}}\,\frac{x}{\cos\Theta} - \frac{\sin\left[(2\pi f\sqrt{m/2eV}\,x)/\cos\Theta\right]}{2\pi f}\right) - x\tan\Theta$$

where $V = 1.333 \times 10^{11}$ E.M.U.
$f = 5 \times 10^{6}$
$\Theta = 16^\circ\ 10.1'$
$a_1 = 8 \times 10^{10}$ E.M.U.
$x_{\max} = 25.21$ cm.

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[3] For instance, the necessity for the correct displacement of S_2 from the plane half way between the condenser plates of a, so that the ions will enter the analyzing condenser just when $E_y = 0$, will cause some difficulty, no doubt.

thermore, it is obvious that harmonics will only distort the mass scale. It is interesting indeed, to find in the second curve the linear relationship $\Delta M/M = \Delta V/V$ for all integral values of M. Here the oscillating terms of the harmonics as well as that of the fundamental will have no effect whatever. This will be true whenever conditions are so chosen to make the oscillating term disappear for some integral value of M as has been done in the calculation of this plot. When there will not be at least one integral value of M for which the arguments of the sine terms are whole multiples of π, the linear relation will no longer hold and the curve of m/e versus V will have the general aspect of the curve presented for the entire mass range including the non-integral M's.

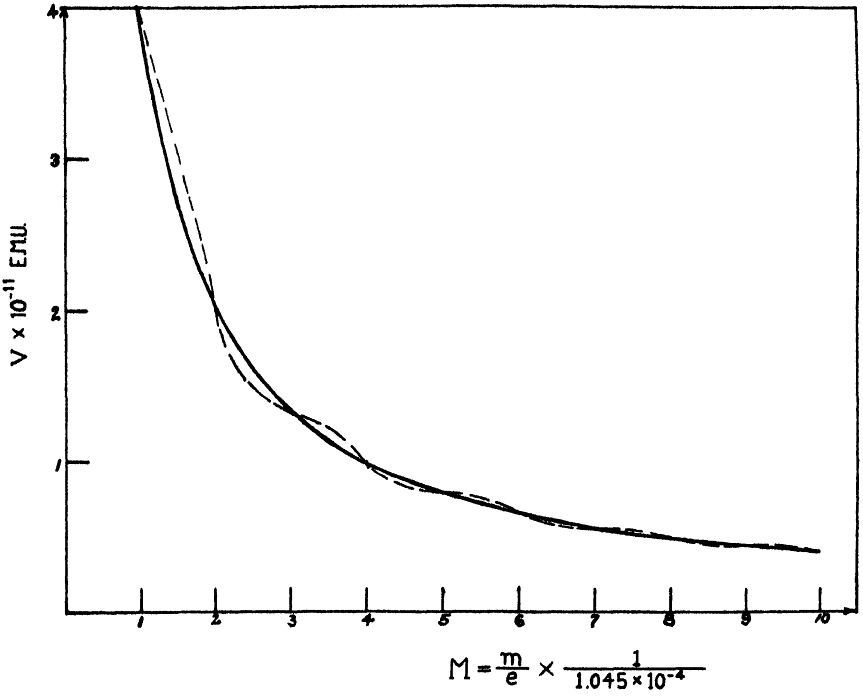

FIG. 3. M/e AS A FUNCTION OF V

Solid curve, considering only integral M's, $V = \frac{a^2}{8\pi^2 f^2 \sin^2\Theta} \quad \frac{1}{m/e}$

Broken curve, considering all values of M, equation 1.

It is evident that a broadening of the peak will result from the fact that even though $\sin 2\pi n f t \neq 0$ but differs very little from it, ions will still enter the analyzing condenser with a definite y component of velocity due to the finite width of the slit S_2. In order to make even a rough estimate, it is necessary to assume a definite form for the field in the small condenser

Below are two curves of this equation where m/e is plotted versus one of the variables (a_1, figure 2; V, figure 3), while the others are kept at the arbitrary values

$f = 5 \times 10^6$
$x = 25.21$ cm.
$\Theta = 16° 10.0'$
$V = 4 \times 10^{11}$ E.M.U. when a_1 was taken as the variable.
$a_1 = 8 \times 10^{10}$ E.M.U. when V was taken as the variable.

In order to plot the second curve, one is obliged to make the substitutions

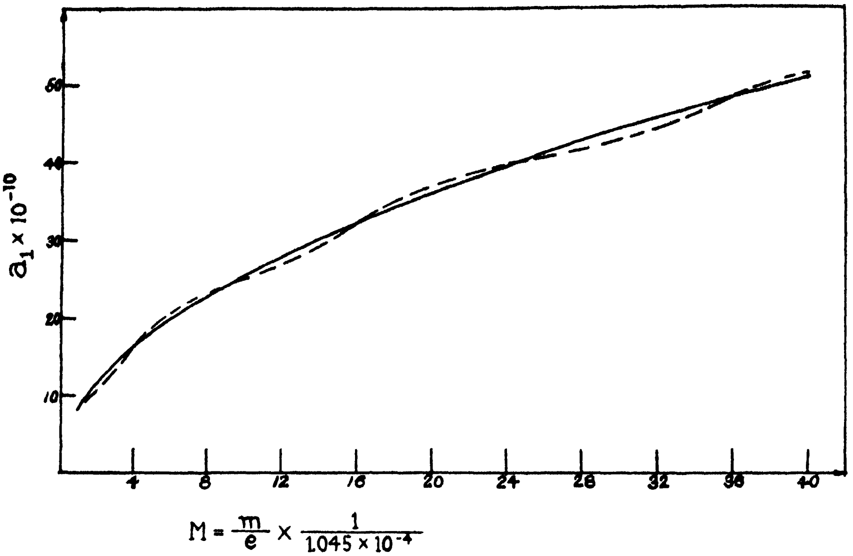

FIG. 2. M/e AS A FUNCTION OF a_1

Solid curve, neglecting sine term, equation $a_1 = \sqrt{8\pi^2 f^2 V \sin^2\Theta\, m/e}$
Broken curve, considering sine term, equation 1.

$\sqrt{m/e} = 1.022 \times 10^{-2}\alpha$ and $\sqrt{1/2V} = 1.118 \times 10^{-6}\beta$ and set $\alpha\beta = k$. He can then solve for $1/\beta^2$ in terms of k, i.e.,

$$\frac{1}{\beta^2} = \frac{V}{4 \times 10^{11}} = \frac{7.638 \times 10^{-4}k - 81.04 \times 10^{-6} \sin 3\pi k}{7.638 \times 10^{-4}k^2}$$

and on assigning definite values to k, can obtain the corresponding $V(\beta)$, whence he can calculate the necessary m/e. In similar manner one can find m/e as a function of Θ, f, or x.

These curves permit us to make the important conclusion that, owing to the small amplitude of the oscillating term, m/e will be a monotonic function of each of the variables so that there is no danger of obtaining ghost peaks or the possibility of several peaks coming at the same point. Fur-

As indicated in the diagram, Θ is so chosen as to make $y = 0$ at a given x. Thus is the condition stated in assumption (2) assured.

It is to be noticed that the value of y depends on linear terms in x upon which are superposed small oscillatory terms whose maximum values are between 0.1 and 0.05 of the values of the corresponding linear ones for the frequencies used. The effect of the oscillating part diminishes very rapidly for the higher harmonics, since their amplitudes are proportional to $1/n^2$. Were we to neglect these smaller terms, we would obtain the relation

$$e/m = 8\pi^2 f^2 V \sin^2 \Theta / a^2$$

where

$$a = \sum_{n=1}^{\infty} \frac{a_n}{n}$$

and

$$\frac{\Delta m}{m} = \frac{2\Delta a}{a} = -\frac{2\Delta f}{f} = -\frac{\Delta V}{V} = \frac{2\Delta\Theta}{\tan\Theta}$$

from which it is obvious that: (a) the presence of harmonics serves only to affect the value of Θ initially chosen to make $y = 0$. (b) For large angles there will be slight directional focusing due to the fact that cot Θ does not change rapidly then. (c) e/m is independent of x. (d) There are enough variables in this arrangement so that one can adjust any mass range to come in a convenient range of experimentation.

That the effects of neglecting the oscillating terms are small in certain cases, can readily be seen from the following calculations made with the last expression:

Atomic weight	100	30	1
e/m (in E.M.U.)	95.7	319	9570
V, accelerating voltage (E.M.U.)	8×10^{10}	8×10^{10}	4×10^{11}
f, frequency of fundamental	5×10^{5}	1×10^{6}	5×10^{6}
a (in E.M.U.)	8×10^{10}	8×10^{10}	8×10^{10}
x (in cm.)	20.0	20.0	20.0
sin Θ	0.6231	0.5679	0.2784
Θ	38° 32.5′	34° 36.5′	16° 10 0′
$\dfrac{\text{linear term}}{\text{amplitude of oscillating term}}$	20.5	21.4	7.48

On the other hand, when the amplitudes of the harmonics become negligibly small, one can retain the sine term obtaining the relationship.

$$\frac{m}{e} x \tan\Theta - \frac{a_1 x}{2f\cos\Theta}\sqrt{\frac{m}{2eV}} + \frac{a_1}{(2\pi f)^2}\sin\left(\frac{2\pi f x}{\cos\Theta}\sqrt{\frac{m}{2eV}}\right) = 0 \qquad (1)$$

oscillating circuits has reached such a stage of development that it is not difficult to obtain an almost pure sine wave in the frequency range desired. (4) Work done with mass spectrographs as of the Dempster type, in which homogeneity in accelerating voltage of the ions is assumed, has apparently been quite successful (3). (5) Since deviations from the simple equations derived here will only distort the mass scale slightly, calibrations with a series of known gases will circumvent the difficulty.

Consider the arrangement shown in figure 1.

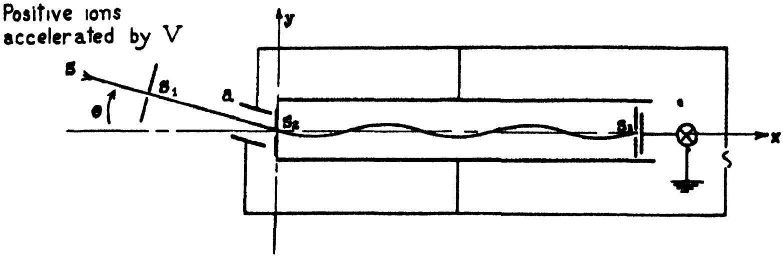

Fig. 1. Arrangement of the Mass Spectrometer

The equations to be solved are:

$$\ddot{x} = \ddot{z} = 0$$

$$\ddot{y} = E_y e/m$$

where

$$E_y = \sum_{n=1}^{\infty} a_n \sin 2\pi n f t$$

with the initial conditions:

$$\left.\begin{aligned} \dot{x}_0 &= \sqrt{2eV/m}\cos\Theta \\ \dot{y}_0 &= -\sqrt{2eV/m}\sin\Theta \\ \dot{z}_0 &= 0 \end{aligned}\right\} \quad \begin{gathered} \text{at} \\ x = y = z = 0 \\ \text{and} \\ t = 0 \end{gathered}$$

i.e., the ions enter the field when the argument of the sine terms is a whole multiple of π (hence the necessity of the small condenser, a, which is to act as a valve). The solutions obviously are

$$x = (\sqrt{2eV/m}\cos\Theta)t$$

and

$$y = \frac{e}{m}\left(\sqrt{\frac{m}{2eV}}\,\frac{x}{\pi f\cos\Theta}\sum_{n=1}^{\infty}\frac{a_n}{2n} - \frac{1}{\pi^2 f^2}\sum_{n=1}^{\infty}\frac{a_n}{(2n)^2}\sin\left(\frac{2\pi f n x}{\cos\Theta}\sqrt{\frac{m}{2eV}}\right)\right) - x\tan\Theta$$

A SIMPLE MASS SPECTROMETER

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It had long been thought desirable to use a mass spectrograph (particularly the type that allowed the direct measurement of intensities of the ions produced by electrons of known energy) for the analyses of substances having a small vapor pressure (0.001 mm. of mercury or higher). These analyses would be of value from a purely chemical point of view as well as from the physicochemical aspects involved in the determination of bond energies, the energetics of certain reactions, etc. The labor and cost of setting up the usual more refined types of spectrographs[1] makes one feel that the general applicability of this apparatus has been somewhat restricted on that account. An outstanding situation has arisen, due to the discovery of deuterium, which impressed many chemists that numerous problems in that field could be more easily solved by the use of such an instrument. It is proposed that a simple mass spectrometer can be constructed, based on a principle first discussed by W. R. Smythe (4) and later made use of by him and Mattauch in the development of an efficient velocity filter for ions (1, 2, 5, 6).[2]

The experimental arrangement here suggested differs from the above in that the oscillating field is directly made to be the mass analyzer, it being assumed in this discussion that a condenser can be treated as ideal, i.e., one which produces a uniform field ending sharply at its geometrical boundaries, that the wave-form of the oscillating field is a definitely known odd function, and that the ions to be analyzed are uniformly accelerated (homogeneous in voltage drop).

For the simplified arrangement suggested, these assumptions can be justified. (1) The condenser plates are to be placed close together, so that the inhomogeneous region (equal approximately to three times the distance between the plates) will be limited to a small fraction of the total distance traveled. (2) The ions will travel in a path deviating but slightly from the plane half way between the plates. (3) The technic in designing previous paper shows the very large effect of the acid upon the oxidation potential of the ferri–ferrocyanide system.

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[1] An excellent summary of the methods of mass spectroscopy describing various arrangements of fields which will produce the desired focusing in directions and velocities of the ions is given by Mattauch (Physik. Z. **35**, 567 (1934)).

[2] Such an application was indicated by him; see reference 4, p. 1285.

SUMMARY

The fourth ionization constant of ferrocyanic acid was found to be equal to 5.6 × 10^{-5} at 25°C.

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$$E = \epsilon_0 + 0.0591 \log \frac{c_{Fe(CN)_6^{---}}}{c_{Fe(CN)_6^{----}}} + 0.0591 \log \frac{f_3}{f_4}$$

In the mixture without acetic acid $c_{Fe(CN)_6^{----}} = 0.0004$; in the mixture with acetic acid (table 1) $c_{Fe(CN)_6^{----}} = x = 0.0004 - HFe(CN)_6^{---}$. From the difference in oxidation potential between the two mixtures, being 0.4156 − 0.3867 = 0.0289 volt, it is easily found that:

$$0.0289 = 0.0591 \log \frac{0.0004}{x}$$

$$x = 1.29 \times 10^{-4}$$

and

$$c_{HFe(CN)_6^{---}} = 4 \times 10^{-4} - 1.29 \times 10^{-4} = 2.71 \times 10^{-4}$$

From the known normal potential ϵ_0 and the value of the oxidation potential of 0.3867 volt in the mixture being 0.01 molar in sodium acetate a value for f_4/f_3 of 0.30 is derived.

Therefore

$$K_4 = \frac{4.06 \times 10^{-4} \times 1.29 \times 10^{-4}}{2.71 \times 10^{-4}} \times 0.30 = 5.8 \times 10^{-5}$$

In table 1 the results of the measurements and calculated values of K_4 are reported in mixtures containing 0.01 mole of sodium acetate and varying concentrations of acetic acid. The measurements were repeated using a series of potassium acid phthalate buffers with hydrochloric acid. The analytical concentration of the potassium salt was 0.05 molar. In the calculation of f_4/f_3 it is assumed that potassium biphthalate (not considering the pH effect) has the same effect upon the oxidation potential of the ferrocyanide–ferricyanide mixture as potassium chloride has at the same ionic strength. This assumption is justified by the fact found in the previous paper, that the "salt effect" upon the oxidation potential is virtually independent of the kind of anion in dilute solutions. The values of K_4 reported in table 2 decrease with increasing hydrogen-ion concentration of the mixture. This is to be attributed to a specific effect of the hydrogen ions upon the potential of the ferro–ferricyanide electrode. No correction has been applied, since this effect is not quantitatively known. Still there is a very good agreement between the average values of K_4 found in tables 1 and 2, the total average being 5.6×10^{-5} at 25°C. Measurements were also made in mixtures containing various concentrations of hydrochloric acid. In this case insufficient data were available for the computation of K_4, and only the values of the oxidation potentials found are reported in table 3. Comparison of these figures with those given in table 4 of the weight of the colloid. W is obtained from the knowledge of the equivalents of hydrochloric acid originally added to the system and the equivalents of hydrogen ion remaining in the system at equilibrium, according to the equation

$$W = \frac{\text{Total HCl added (equivalents)} - \left[\left([\mathrm{H}^+]_i \cdot \frac{V_i}{1000}\right) + \left([\mathrm{H}^+]_o \cdot \frac{V_o}{1000}\right)\right]}{A}$$

The percentage ionization of the protein chloride is given by the ratio α'/W.

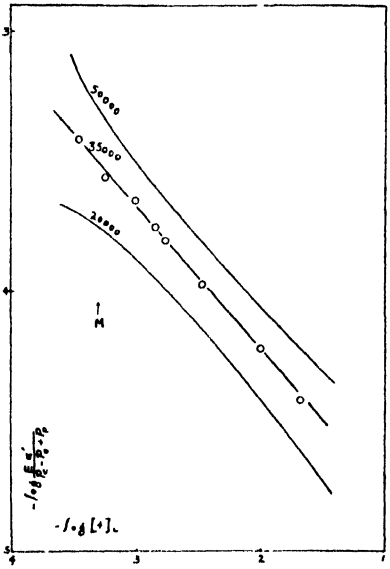

FIG. 1. OVALBUMIN

Any osmotic pressure due to the protein molecule, P_p, must be subtracted from the observed osmotic pressure, P_o, in order to obtain the fractional osmotic pressure due to the diffusible ions, before this can be analyzed to find if the same relationship exists when the colloid is a protein as has been found to exist for gum arabic. The value of P_p is obtained from the equation,

$$P_p = \frac{A/V_i \cdot 10^3 \cdot 25280}{M}$$

where M is the molecular weight of the protein. Plotting $\log \frac{E\alpha'}{P_c - (P_o - P_p)}$ against $\log [(\mathrm{H}^+) + (\mathrm{Na}^+)]_i$ should give a straight line if the proper value for M is chosen and if the relationship found in the case of the gum arabate also holds for the diffusible ions in the system containing the protein. If too high a value for M is chosen in calculating P_p, when the above factors are plotted a curve will be obtained convex in one direction; if M is too

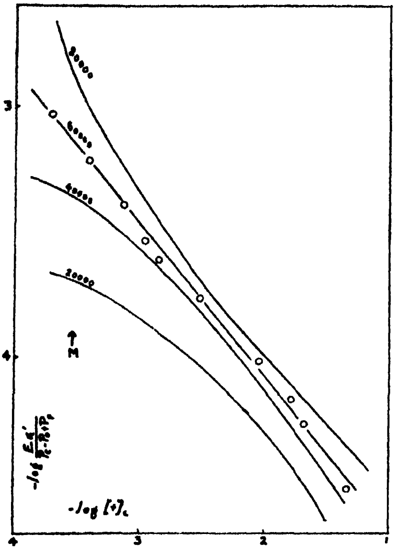

FIG. 2. COW SERUM ALBUMIN

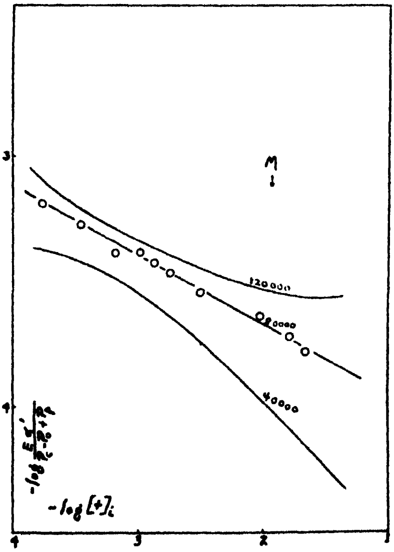

FIG. 3. HORSE SERUM ALBUMIN

small a curve will be obtained which is convex in the other direction, and the proper value of M will give a straight line lying between these curves, as is shown by the figures.

DISCUSSION

Figures 1, 2, and 3 show the plotted values of log $\frac{E\alpha'}{P_c - P_o + P_p}$ against log $(+)_i$ for the experiments with egg albumin, cow serum albumin, and horse serum albumin, respectively. In each, varying values of M, the molecular weight of the protein, are used in calculating P_p. The graphs show straight lines when M is of the order of 35,000 for egg albumin, of 60,000 for cow serum albumin, and of 80,000 for horse serum albumin. Other values for M in each case give curved lines, the assumed values for M being indicated thereon.

The values for the molecular weights of egg albumin and horse serum albumin as determined by other methods are of the same order of magnitude as those for which straight lines are obtained in these graphs. This can be taken as proof that the empirical relationship found to exist for osmotic pressures derived from diffusible ions in the case of gum arabic solutions, holds also for protein solutions where the colloidal molecules are of sufficiently small dimensions to exhibit an appreciable osmotic pressure of their own. Also, it appears that the molecular weights and osmotic activities of the colloids under the conditions of the present experiments are not markedly different from those shown at the isoelectric point and in the absence of a Donnan equilibrium.

It cannot be claimed that this method is an accurate one for the determination of molecular weights of colloid electrolytes. So many calculations are involved that a small experimental error becomes a relatively large variation in the final values of $\frac{E\alpha'}{P_c - P_o + P_p}$. A change in M of over 15 per cent (greater at higher values of M) would be required before the straightness of the plotted line would be definitely destroyed. The method can, therefore, give only an approximation of the molecular weight of the colloid. The experiments show clearly that when the colloid osmotic pressure is corrected for, the relationships found to exist for osmotic pressures resulting from the unequal distribution of ions across the membrane in the case of gum arabic also hold in the case of proteins, where the molecules of colloid offer an appreciable fraction of the total osmotic pressure of the colloid-containing solutions. The membrane acts truly semipermeable for the colloid, which is retained mechanically from passing through, and its osmotic activity is proportional to its concentration difference across the membrane. For the diffusible ions, the equilibrium unequality across the membrane is due to electrostatic forces and not mechanical obstruction. The osmotic pressure due to these ions is not proportional to their total concentration difference across the membrane. The deviation ($P_c - P_o$) from this expected proportionality is proportional to the same factors as found in the gum arabic experiments. A theoretical basis for this obscured relationship has not yet been arrived at. Until this is done, the significance of slope and intercepts of the straight lines of figures 1, 2, and 3 cannot be given.

The number of equivalents of acid, W, which combine with unit weight of the protein in the various experiments is of interest. In the experiments shown in the tables the total equivalents of acid added were constant and increasing amounts of sodium chloride were added. This increase in salt content of the system caused a decrease in R, the ratio of distribution of ions across the membrane, thus causing a higher hydrogen-ion concentration to exist inside of the membrane, with a consequent greater binding of hydrochloric acid by the protein. The degree of ionization, α'/W, of this protein chloride appears to be only of the order of 50 to 60 per cent under the conditions of these experiments. In other experiments, the data for which are not included in this paper, it becomes apparent that as the pH of the protein solution is varied progressively away from the isoelectric point of the protein, W increases rapidly through the first increments of pH and then more slowly as saturation is reached in solutions of high acid content. At the same time the value of α'/W increases slowly at first then more rapidly, until in solutions of high acid content (i.e., most distant from the isoelectric point) the degree of dissociation approaches 100 per cent. This means that protein salts act as progressively stronger electrolytes as the pH of their environment deviates from the isoelectric point of the protein. From this it would be expected that the degree of ionization of the "Zwitterion" in the isoelectric protein solution would have a very low percentage of the total possible ionizable groups actually ionized.

SUMMARY

An empirical relationship which had already been found to exist for gum arabic solutions in defining the deviation between the observed osmotic pressure (P_o) and the calculated osmotic pressure (P_c) due to the unequal distribution of diffusible ions, is found to hold for protein solutions when correction is made for the osmotic pressure due to the colloid itself. (With gum arabic the size of the micellae was so large as to be negligible in comparison with that due to the diffusible ions.) Conversely, if this empirical correction for the osmotic pressure due to the diffusible ions is assumed to hold for protein solutions, it becomes possible to determine the molecular weights of the proteins in dilute solutions and in solutions having hydrogen-ion concentrations other than those at the isoelectric points of the proteins.

Three proteins were subjected to this analysis. Molecular weights were found to be 35,000, 60,000, and 80,000 (±ca. 15 per cent) for crystallized egg albumin, uncrystallized cow serum albumin, and crystallized horse serum albumin, respectively.

This relationship for the protein solutions is

$$\frac{E\alpha'([\pm]_i)^x}{P_c - P_o + P_p} = \text{a constant}$$

(at all values of hydrogen-ion, salt, and colloid concentrations) where:

P_o = observed osmotic pressure.

P_c = osmotic pressure (calculated) on basis of unequal distribution of diffusible ions.

P_p = osmotic pressure (calculated) due to protein of molecular weight = M.

E = 59.1 ($\text{pH}_o - \text{pH}_i$) = the membrane potential.

α' = equivalents of diffusible ion derived from unit mass of the protein.

$[\pm]_i$ = concentration of all ions, bearing same sign of charge as the protein, in the colloid-containing solution, i.e., foreign salt concentration inside the membrane.

x = a constant for a given colloid.

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INFLUENCE OF GASES ON SILVER SOLS

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In a previous paper (3) gases were found to have a stabilizing effect on Zsigmondy gold sols toward electrolytes, but no increase in charge was observed by measurement of cataphoretic velocity. The increase in stability was observed only with sols which apparently contained secondary particles. The study has been extended to other colloidal systems, and the results on silver sols are reported in this paper.

PREPARATION OF SOLS

Bredig silver sols

Bredig silver sols were prepared by the usual method of maintaining an arc between two silver electrodes. By use of a dismantled microscope for feeding the wire and a large inductance coil (1), a steady arc could be maintained. Owing to the formation of gases and the high per cent of silver oxide (8), Bredig silver sols were not entirely satisfactory for this investigation. Our experience in the preparation of other than a very dilute sol is not in accord with that of Best and Cox (2), who report no difficulty in preparing sols in water with a specific conductivity of 0.4 to 0.6×10^{-6} mhos. Difficulty was also encountered in preparing a sol of sufficient concentration for our studies by use of freshly purified sodium hydroxide at the optimum concentration reported by Pauli and Perlak (6). However, sodium hydroxide which had been standing in glass bottles gave good results. This led to an investigation which showed that sodium silicate in concentrations as low as 6×10^{-7} *N* produced a comparatively stable silver sol. Water which had been standing in soft glass bottles a short time or in Pyrex bottles for twenty to thirty days gave similar results. Consequently a study was made by one of the authors (7) to determine the extent and effect of the solution of glass from bottles under laboratory conditions.

Kohlschütter silver sols

These sols proved to be unsuitable for the study of the influence of gases on their properties, because hydrogen is used in the reduction of the silver oxide solution. Since silicates dissolved from glass were found to affect the stability of Bredig sols so markedly, it was thought that greater amounts of silicates would be dissolved at the higher temperatures used for reduction in Kohlschütter's method (50–60°C.) and would contribute much more to the sols' properties than has generally been attributed. Accordingly a rather extended study was made on the influence of surface and solubility of glass on these sols, but before the completion of this work a paper by Weiser and Roy (10) was published which corroborates the results obtained in this laboratory.

TABLE 1

Effect of bubbling gases on the precipitation value of silver sols

SOL NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	METHANE	ETHYLENE
Bredig 2	7.0	13.0	11.0	5.0		
3	8.0	14.0	14.0	6.0		
4	10.0	17.0	18.0	2.0		
5	22.0		23.0	12.0		23.0
Formol 1	7.0	20.0	20.0	22.0	32.0	34.0
2	20.0	32.0	28.0	34.0	42.0	45.0
3	34.0		38.0	44.0		44.0
4	40.0	40.0	40.0	40.0		40.0
5	42.0	42.0	43.0	43.0	42.0	42.0

TABLE 2

Effect of gas pressure on precipitation value of silver sols

SOL NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	METHANE	ETHYLENE
Bredig 1	7.0	12.3	10.0	5.0		
4	10.0	14.5		2.5		
Formol 1	7.0	12.0		16.0	20.0	18.0
2	20.0			28.0	28.0	30.0
4	40.0	40.0		40.0		40.0

Formol silver sols

Silver sols prepared by reduction of silver nitrate in the presence of a small amount of bromide or iodide with formaldehyde as described by the authors (8) proved to be particularly suited to the study of the effect of gases on their properties.

RESULTS

In order to study the influence of gases on the sols, measurements were made of their precipitation values, cataphoretic velocities, and conductances before and after treatment. Precipitation values were measured by diluting varying volumes of 0.1 *N* sodium nitrate to 15 cc. and mixing quickly with 10 cc. of the sol by use of a tube made as described by Weiser and Middleton (9). Cataphoresis measurements were made by the Burton moving boundary method in a set-up similar to that suggested by Kruyt and van der Willigen (4), and calculations were made as previously described (3).

TABLE 3

Effect of treatment on stability of silver sols

FORMOL SOL NO.		ORIGINAL SOL CORKED TIGHT	METHANE BUBBLED	STIRRING WITH MOTOR IN CORKED, FILLED FLASK	BOILING UNDER VACUUM	SHAKING IN FLASK OPEN TO AIR	STANDING OPEN TO AIR
6	Precipitation value	8.0	22.0	10.0	2.0	20.0	12.0
	Color	Milky green	Yellow	Yellowish green	Green	Yellow	Greenish yellow
7	Precipitation value	6.0	28.0	8.0	Precipitate	20.0	10.0
	Color	Milky green	Yellow	Yellowish green		Yellow	Greenish yellow

TABLE 4

Effect of gases on cataphoretic velocity of silver sols

Values in cm./sec./volt/cm. × 10^5 at 25°C.

SOL NO	ORIGINAL	OXYGEN		NITROGEN		HYDROGEN		METHANE		ETHYLENE	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Bredig 3	48	48		47	42						
4	41	41	47	41	46	40	41				
Formol 1	41	41	42			41	41	40	41	41	42
3	42	43	42			41	42	43	41	41	42
4	40	40	41	41	40	41	40	40	41	40	

(a) Gas bubbled through sol for 3 hours.
(b) Two atmospheres gas pressure.

Gases were run through the silver sols in well-leached Pyrex Erlenmeyer flasks for a period of about three hours, which was sufficient to give the maximum effect. The effects of gases on the Bredig and the formol silver sols are given in table 1. A portion of the sol was kept in a completely filled and tightly corked flask on which tests were made for the original value. The precipitation values are all given in millimoles of sodium nitrate just necessary to cause precipitation.

To determine whether the stabilizing action was due to the agitation or to the presence of gases, samples of the same sols were treated with gases under a pressure of 2 to 3 atmospheres for the same length of time. In general, gases under pressure stabilized the sol, but the effect was not as great as that caused by bubbling. The results are tabulated in table 2.

Experiments, as tabulated in table 3, were carried out to determine whether agitation alone, in the absence of gases, increased the stability.

The results of the cataphoresis measurements are given in tables 4 and 5. Table 4 gives a summary of some of the results for different gases, and table 5 gives detailed values taken during the measurements on two of the sols treated with hydrogen and methane respectively. Table 6 gives some of the results of conductance measurements before and after treatment with gases.

TABLE 5

Effect of methane and hydrogen on cataphoretic velocity

FORMOL SOL NO. 3	TIME IN MINUTES	VOLTS	DISTANCE BETWEEN ELECTRODES IN CM	DISPLACEMENT TOWARD POSITIVE POLE IN CM. (UP)	DISPLACEMENT AWAY FROM NEGATIVE POLE IN CM. (DOWN)	VELOCITY IN CM / SEC./VOLT/ CM × 10^5
Original	20	70	28.6	1.35	1.05	40.9
Hydrogen	20	70	28.6	1.20	1.20	40.9
Methane	20	70	28.6	1.25	1.20	41.7
Methane, pressure	20	70	28.6	1.30	1.15	41.7

TABLE 6

Effect of gases on conductance of silver sols

Values in mhos × 10^6 at 25°C.

SOL NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	HYDROGEN PRESSURE	ETHYLENE
Bredig 3	35.5	32.4	32.5	19.6	26.9	
4	49.2	48.4	49.0	26.3	33.0	
Formol 1	423	422		423	422	
2	453	452	452	453		452
4	511	511	512	511	511	512

DISCUSSION

The results given above show that the presence of gases produced a stabilizing effect on the silver sols except in the case of Bredig sol No. 5 and formol sols Nos. 4 and 5. Bredig sol No. 5 was made by adding slightly more sodium silicate than the amount necessary to produce a sol of fair concentration. Formol sols Nos. 4 and 5 were made by adding 5 cc. and 10 cc. of 0.01 *N* potassium bromide compared to 1.75 cc., 2.0 cc., and 2.5 cc. of 0.01 *N* potassium bromide for sols 1, 2, and 3 respectively. Formol sols Nos. 4 and 5 were yellow and clear by transmitted light, indicating a high and uniform degree of dispersion. The other three sols were cloudy and milky green when prepared and remained unchanged on standing in a stoppered flask. Bubbling gases through the cloudy sols changed the color from milky green to a clear yellow, indicating a higher and more uniform degree of dispersion. No effect on the color of the yellow sols having the larger amounts of potassium bromide was discernible after treatment with gases. Thus, it appears that gases affect only those sols which are on the border line of stability and which apparently contain secondary particles, that is, an agglomeration of two or more primary particles. If less than 1.75 cc. of 0.01 *N* potassium bromide was used, the sol was unstable, and gases would not stabilize it. Gases apparently do not take the place of stabilizing ions. Hydrogen decreased the stability of Bredig silver sols, owing to reduction of silver oxide and hydroxide as shown by conductance measurements in table 6.

A much larger number of experiments were made than those given in the tables, and in many of these the amount of electrolyte necessary for complete precipitation of *all* of the colloid in some of the milky green sols which had been tightly corked was rather high, even though 1 cc. to 2 cc. caused more than two-thirds of the colloid to settle out. This partial precipitation would indicate an inhomogeneous sol. In the case of the yellow sols greater uniformity was shown, because complete precipitation occurred when the characteristic color change was produced. More vigorous stirring during preparation should, therefore, tend to form a more homogenous sol.

The cataphoretic velocity measured and calculated as above is apparently not changed, within the limits of error, by treatment with gases. However, examination of the displacements in the positive and negative arms of the tube before and after treatment with gases as given in table 5 showed that there had been a change either in the electrical nature or in the size of the particles. Settling of the larger particles in the negative arm should tend to even up the displacements, so the effect was not due to a change in the size of the particles; moreover, since the conductance of the sols remained unchanged, the effect was due to differences in distribution of charges on the particles.

In all cases the sum of the displacements was the same within the limits of error in reading the boundary, but the displacement upward toward the positive pole for the original sol was 1.35 cm. while the displacement downward away from the negative pole was 1.05 cm. After treatment by bubbling gases, and for the yellow sols in general, the displacements were more nearly even, about 1.2 cm. in each arm. This indicates that before treatment some of the particles had a higher negative charge than others and were attracted to the positive pole faster than the less negative ones were repelled by the negative pole, thus giving different values for the displacements. After treatment with gases, it appears that the particles all had nearly the same charge. A redistribution of stabilizing ions must have resulted from the agitation during treatment with gases. This conclusion is borne out by the observations given in the previous paragraph on their behavior during precipitation. These observations show that the moving boundary method of determining cataphoretic velocity makes it particularly useful in obtaining the *average* charge on the colloidal particles. If the above explanations are true, then the contentions of Mukherjee (5) that the upper liquid used should always be adjusted so that the displacements of the upward and downward moving boundaries are the same are not entirely justified in all cases.

Since the values in table 3 show that agitation alone will not produce the increase in stability or effectively cause as even a distribution of stabilizing ions as treatment with gases, it may be assumed as in the previous paper (3) that the gases are adsorbed in a layer on the surface of the particle, thus modifying adsorption of ions from the precipitating electrolyte. Only those sols on the border line of stability are affected by gases. This apparently means that they furnish some surface on which the gases may be adsorbed. By use of larger amounts of potassium bromide the surface may be covered with the more strongly adsorbed layer of bromide ions. This is in accord with the theories of poisoning of catalytic surfaces. Just why the agitation in the presence of gases should cause a more uniform and more permanent distribution of stabilizing ions, we are not fully prepared to explain. However, in the presence of gases it may be assumed that as soon as secondary particles are broken up the adsorbed gas prevents re-formation of secondary particles. Also if the presence of a gas is not accompanied by agitation, the secondary particles may not be as readily broken up, and contact between the gas and the surface of the particle is limited.

SUMMARY

1. A discussion of the methods and difficulties involved in preparing silver sols has been given.

2. The influence of gases on silver sols treated in various ways has been determined by measurement of precipitation values, cataphoretic velocities, conductances, and color changes.

3. Gases seem to have a stabilizing effect on those sols which are on the border line of stability and which apparently contain secondary particles. Agitation with gases produces a uniform distribution of stabilizing ions giving an apparently homogeneous sol. When the secondary particles are

broken up, the adsorbed gas apparently prevents their re-formation. No increase in the *average* charge of the particles was observed by measurement of cataphoretic velocities.

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THE ELECTRIC MOMENTS OF SOME ORGANIC COMPOUNDS

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Many para-disubstituted benzene derivatives, like *p*-dichloro- and *p*-dinitrobenzene, have zero moments. This zero moment is to be expected if the benzene ring is flat, since the two substituted dipoles are exactly equal and act in diametrically opposite directions. That certain para compounds with identical groups do possess a definite dipole moment was first discovered by Hassel and Naeshagen (4). They report the moment of the *p*-phthalaldehyde molecule to be 2.85×10^{-18} E.S.U., but they offer no explanation for the apparent abnormal behavior.

This apparent anomaly has been explained by Bergman and Engle (1) on the basis of the theory that the moment of the aldehyde group does not act along the line joining the group to the benzene nucleus. Hence, considering the possibility of free rotation about the bond, the two vector moments may, or may not, act at an angle of 180°, as was previously supposed in all para compounds.

This type of anomalous moments has since been found to be a common characteristic of all molecules containing an —OR group attached to the benzene nucleus, where R may be a hydrogen atom, an alkyl group, an acyl radical, or groups containing oxygen, like —CHO and —COOR. It also occurs when the substituted groups are $—NH_2$, —NHR, or $—NR_2$.

The present paper contains the results obtained from a study of the electric moments of some substituted benzaldehydes, of the three ethanolamines, and of 2-ethylhexanol-1 and the corresponding aldehyde.

APPARATUS AND MATERIALS

The dielectric constants of the solutions were measured by the usual heterodyne beat method, using dynatron oscillators (3) for both variable and constant frequency circuits. The circuit diagram, shown in figure 1, was chosen because of its demonstrated frequency stability. The measuring cell, figure 2, consists of two gold-plated brass discs, one rigidly fixed and the other mounted on the end of a micrometer screw. With this arrangement the position of the plates may be changed and precisely duplicated. The plates were suspended from a tight-fitting Bakelite disc, which also serves as the cover of the Pyrex jar containing the solution under investigation.

The densities were determined by means of a 30-cc. Ostwald-Sprengel pycnometer and are accurate to one part in 300,000. The refractive indices of the liquids were measured by means of a large Pulfrich refractometer provided with a heating device. All measurements were made at 25°C. ± 0.01°. The weighings were made with certified weights and were corrected for air buoyancy.

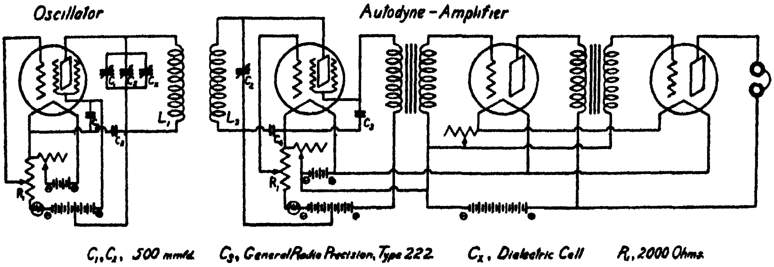

FIG. 1. THE CIRCUIT DIAGRAM

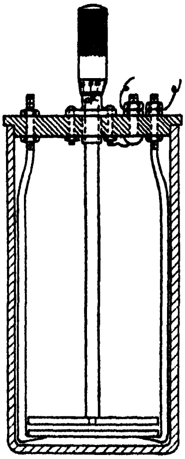

FIG. 2. THE MEASURING CELL

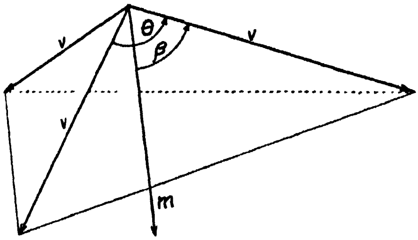

FIG. 3. THREE-VECTOR DIAGRAM

The benzene was made thiophene-free and then carefully purified in the approved standard way. It was finally dried over sodium wire, fractionally distilled, and fractionally crystallized. The boiling point of the middle fraction obtained by distillation through a Loveless column (7) was 80.1°C. at 760 mm.; its freezing point was 5.4°C. Commercial 1,4-dioxane was carefully purified by the method of Kraus and Vingee (6). The final distillation gave a middle fraction boiling at 101.3°C. at 760 mm.

The various aldehydes used were either Eastman's highest grade products, or they were specially prepared in our Division of Organic Manufactures under the direct supervision of Dr. George H. Coleman. They were further purified by accepted methods. Commercial triethanolamine from the Carbide and Carbon Chemicals Corporation was fractionally distilled under reduced pressure, using a small still of the Loveless type (7), modified for operating at reduced pressures. Repeated fractionation yielded the three pure amines. Their boiling points were: monoethanolamine, 65.0°C. at 5 mm.; diethanolamine, 134.0°C. at 3 mm.; triethanolamine, 175.0°C. at 2 mm.

The 2-ethylhexanol-1, also obtained from the Carbide and Carbon Chemicals Corporation, was first treated with metallic sodium wire to remove water and the lower alcohols. It was then fractionally distilled, and the middle fraction boiling at 185.5°C. at 760 mm. was retained. The α-ethylcaproaldehyde, from the same company, was dried over phosphorus pentoxide and fractionally distilled; its b.p. was 163.4–163.5°C. at 760 mm. Dioxane was used as the solvent for the three ethanolamines and *p*-bromo- and *p*-hydroxy-benzaldehyde, while benzene was the solvent for the remaining compounds.

EXPERIMENTAL

The experimental data are collected in table 1. Here, N_2 is the mole fraction of the dissolved substance, K is the dielectric constant, and d is the density of the solutions. Each value given is the mean of several closely agreeing, independent determinations. In table 2 are collected the values obtained for the total polarization, P_∞, the molar refractivity, MR_D, and the electric moment, μ, of the compounds studied.

The total polarization was calculated by means of the equation (5):

$$P_\infty = \frac{K_1 - 1}{K_1 + 2}\frac{1}{d_1}\left(M_2 - \frac{d - d_1}{N_2}\cdot\frac{M_1}{d_1}\right) + \frac{3M_1}{d_1(K_1 + 2)^2}\cdot\frac{K - K_2}{N_2}$$

where the subscript 1 refers to the pure solvent, subscript 2 to the pure solute, and the symbols without subscript refer to the solution of mole fraction N_2. The molar refractivities were calculated by means of the Lorenz–Lorentz equation

$$MR = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{d}$$

except for the two solid compounds for which the value given is the sum of the atomic refractivities. The dielectric constants are probably accurate to about 0.02 per cent and the densities to 0.005 per cent. Because of its limited solubility in dioxane, the electric moment of monoethanolamine was calculated from data on a single solution. Except for this one substance, the electric moments of the compounds are probably correct to within 1 per cent.

TABLE 1

The dielectric constants, densities, and mole fractions of solutions of certain aldehydes and ethanolamines in benzene and dioxane at 25°C.

N_2	K	$d_{4°}^{25°}$	N_2	K	$d_{4°}^{25°}$	N_2	K	$d_{4°}^{25°}$
p-Bromobenzaldehyde			*p*-Hydroxybenzaldehyde			*p*-Methoxybenzaldehyde		
0.04564	2.533	1.06185	0.04039	3.255	1.03659	0.05439	3.440	0.89152
0.02849	2.412	1.04885	0.02822	2.933	1.03400	0.02992	2.920	0.88324
0.02016	2.351	1.04317	0.01933	2.712	1.03230	0.02070	2.711	0.88010
0.01013	1.288	1.03600	0.00999	2.471	1.02900	0.01104	2.501	0.87674
p-Tolualdehyde			2-Ethylhexanol-1			*α*-Ethylcaproaldehyde		
0.07499	3.462	0.88659	0.04942	2.460	0.86805	0.04820	2.714	0.86863
0.04965	3.062	0.88226	0.02966	2.399	0.86997	0.02957	2.541	0.87086
0.03025	2.751	0.87875	0.01932	2.349	0.87094	0.01950	2.453	0.87146
0.01989	2.584	0.87633	0.00909	2.316	0.87204	0.01095	2.376	0.87230
0.01036	2.434	0.87476						
Triethanolamine			Diethanolamine			Monoethanolamine		
0.03964	2.928	1.03360	0.04514	2.174	1.03070	0.01016	2.288	1.02718
0.02857	2.743	1.03184	0.03261	2.568	1.02976			
0.01990	2.579	1.03074	0.02049	2.450	1.02910			
0.01960	2.577	1.03056	0.00933	2.323	1.02842			
0.00724	2.344	1.02884						

TABLE 2

Molecular polarization, molecular refractivity, and electric moments at 25°C.

COMPOUND	P_∞	MR_D	$\mu \times 10^{18}$ E S U.
p-Bromobenzaldehyde	134.1	35.03	2.19
p-Hydroxybenzaldehyde	396.0	33.38	4.19
p-Methoxybenzaldehyde	345.0	37.95	3.85
p-Tolualdehyde	262.0	36.43	3.30
2-Ethylhexanol-1	103.6	40.45	1.74
α-Ethylcaproaldehyde	183.3	39.19	2.64
Triethanolamine	301.0	37.82	3.57
Diethanolamine	189.9	26.95	2.81
Monoethanolamine	122.0	16.22	2.27

DISCUSSION

Applying the method of Bergman and Engle to the resolution of the moment of *p*-bromobenzaldehyde, we have calculated the angle between the aldehyde group moment and the line joining the 1 and 4 carbon atoms of the ring to be 127°. They also designate by α the angle between the planes in which the two moments lie and which also pass through the 1 and 4 carbon atoms of the benzene ring. This angle was calculated to be 153° for *p*-hydroxybenzaldehyde and 150° for *p*-methoxybenzaldehyde. In these calculations the moments and angles employed for the hydroxyl and methoxyl groups are the values recorded by Bergman and Engle, namely, 1.70×10^{-18} and 1.23×10^{-18} E.S.U., and 83° and 73°, respectively.

The moments of the monoethanolamine and the diethanolamine were calculated from bond and group moments on the basis of the following assumptions: (1) the moment of each of these amines is the vector sum of the N—H and the N—C_2H_4OH bonds; (2) the contribution of each such moment to the total moment is the same, regardless of the other bonds present. Thus, for example, the contribution of one N—H moment to the moment of the molecule is the same in diethanolamine as in ammonia.

From figure 3 it will be observed that for three equal vectors, v with an angle θ between them, each vector contributes one-third to the resultant vector, m. The angle β between any one vector and the resultant is given by

$$\cos \beta = m/3v$$

The angles θ and β are connected by the relation,

$$\sin \theta/2 = (\sqrt{3}/2) \sin \beta$$

If now we assume that the moment of the triethanolamine molecule is the resultant of three hydroxyl moments, each of $\mu = 1.70 \times 10^{-18}$ E.S.U., and acting at an angle θ to each other, this angle may be calculated by the above relations. The calculated value of θ is about 77°. However, the assumption made is not exactly true, since it omits from consideration the contribution of the N—C moment; the resultant error due to its omission is probably not large. We thus obtain a tetrahedral configuration of the vectors with the nitrogen atom at the apex. The angle, β, between each vector and the altitude is found to be 45°.

The angles θ and β were also calculated for the ammonia molecule, using Dennison and Uhlenbeck's values (2) for the interatomic distances, namely, N—H = 1.02 A.U. and H—H = 1.64 A.U. The angles for ammonia are: $\theta = 107°$ and $\beta = 68°$. With these angles and the moment of the ammonia molecule, 1.49×10^{-18}, the moment of the N—H bond was calculated to be 1.33×10^{-18} E.S.U. It is evident then that the N—H vectors for ammonia form a somewhat flatter tetrahedron than do the vectors of triethanolamine.

With these values for the moment vectors and the angles between them and the resultant vector we have calculated the moments of the monoethanolamine and diethanolamine to be 2.19×10^{-18} and 2.87×10^{-18}

E.S.U., respectively. The corresponding values obtained experimentally were 2.27×10^{-18} and 2.81×10^{-18}. In making these calculations it has been assumed that each N—H moment and each N—C_2H_4OH moment contributes the same moment to the total moment of monoethanolamine and diethanolamine that it contributes to the total moment of ammonia and triethanolamine. Considering the assumptions made, the agreement between the calculated and experimental values of the total moments is exceptionally good.

SUMMARY

1. The dielectric constants and the densities of dilute solutions of *p*-bromobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde, *p*-tolualdehyde, 2-ethylhexanol-1, α-ethylcaproaldehyde, triethanolamine, diethanolamine, and monoethanolamine have been measured at 25°C.

2. From these the total polarization and the dipole moments of each of the compounds have been calculated.

3. The spacial orientation of the group moments in the substituted benzaldehydes and in triethanolamine have been calculated.

4. The moments of diethanolamine and monoethanolamine calculated from theoretical considerations agree well with the values determined experimentally.

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A KINETIC INTERPRETATION OF THE COLORING OF GLASS BY X-RAYS[1]

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It is well known that glass becomes colored, usually brown or violet, when it is exposed to x-rays or other ionizing radiation. The color of glass which is exposed to a source of constant intensity increases at first rapidly and then gradually until it finally reaches a constant value, the saturation color. While a great deal of work has been devoted to the study of these effects (7, 12; see also 2, 3, 4, 9, 11), there is relatively little quantitative information[2] available on the rate of coloring of glass by x-rays. In this paper are presented measurements on the relative absorption of visible light as a function of wave length and on the relative absorption of monochromatic light as a function of duration of x-ray irradiation.

EXPERIMENTAL METHOD

Glass samples, 5 cm. square and about 4 mm. thick, were exposed to a Coolidge water-cooled x-ray tube during the routine treatments of patients in the Cancer Institute of the Minnesota General Hospitals. The exposures were not continuous, but consisted of 15- to 30-minute doses separated by 5- to 10-minute intervals. Approximately five hours were given per day. The glass was not exposed at night, nor on Saturday afternoons, Sundays, or holidays.

The deep therapy tube operated on 200 kv. (peak voltage) and 30 ma. current. The glass samples wrapped in black paper were placed inside of the cylindrical lead drum surrounding the tube. They were about 14 inches from the target and under the cathode end of the tube. The x-rays striking the glass were filtered only by the tube itself, except in a few cases where 1 mm. copper was used. The temperature inside of the drum was approximately 25°C.

The color changes were determined in terms of absorption of monochromatic rays in the visible spectrum. A Bausch and Lomb constant

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[1] This work was supported by a grant from the Graduate School of the University of Minnesota.

[2] See, however, reference 6.

deviation spectrometer and a photometer of the Konig-Martin type were used. The absorption of the colored glass was measured relative to that of a clear sample (not irradiated) cut originally from the same piece of glass. The irradiated and non-irradiated samples were interchanged in the photometer specimen holders in order to eliminate partially the errors due to reflection, unequal intensity of the two beams, and lack of perfect adjustment of the "zero" point of the photometer. The glass surfaces were cleaned thoroughly before each set of photometer match points were read. Immediately after each set of readings, the glass was returned to the x-ray protection cylinder and placed in the same position as before.

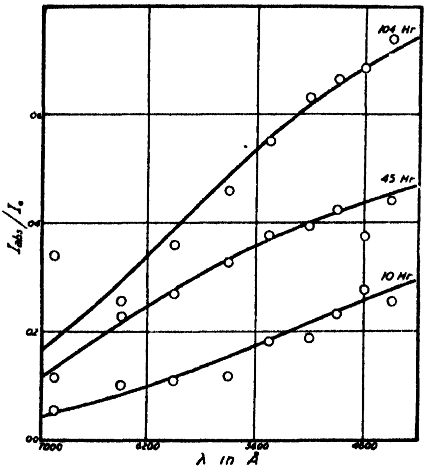

FIG. 1

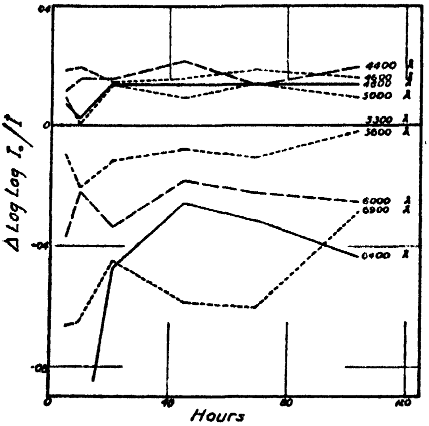

FIG. 2

FIG. 1. RELATIVE ABSORPTION AS A FUNCTION OF WAVE LENGTH

FIG. 2. TEST OF THE HYPOTHESIS THAT THE QUANTITY *cl* IS INDEPENDENT OF WAVE LENGTH

The x-ray intensities at the surface of the glass were the same for most samples. A few pieces of Pyrex, however, were exposed to rays filtered by 1 mm. copper. The intensities of the filtered and unfiltered rays were 45.5 and 185 roentgens per minute, respectively. Twelve per cent of the former and 25 per cent of the latter were absorbed by the glass. These measurements were made by means of a Victoreen Roentgen meter.

DISTRIBUTION OF COLOR

A brownish color, similar to that of commercial amber glass, appeared in all of the samples of glass used, upon irradiation. In figure 1, the relative absorption (I_{abs}/I_0) for a sample of Pyrex is plotted against the wave length of the analyzing light. The three curves correspond to irradiation periods of 10, 45, and 104 hours, respectively.

Probably the simplest interpretation of the change of color with time can be based upon the postulate that the color is due to one substance and that Beer's law applies to the absorption of monochromatic light of all wave lengths studied. On the basis of this assumption we may write[3]

$$\log \left(\frac{I_0}{I}\right)_\lambda = acl \qquad (1)$$

where a is the absorption coefficient, l the thickness of the glass, c the concentration of the colored substance, and I and I_0 the intensities, respectively, of the transmitted and incident light of wave length λ. If at a given time (t) we compare the absorption for two different wave lengths (λ and λ'), we may write

$$\log \log \left(\frac{I_0}{I}\right)_\lambda - \log \log \left(\frac{I_0}{I}\right)_{\lambda'} = \log a - \log a' = \text{constant} \qquad (2)$$

If the relation is obeyed, a plot of

$$\log \log \left(\frac{I_0}{I}\right)_\lambda - \log \log \left(\frac{I_0}{I}\right)_{\lambda,\text{ reference}}$$

against time should consist of one horizontal straight line for each wave length, λ. Such a plot is presented in figure 2, for the same sample of Pyrex which was used in figure 1. It is apparent that the lines show no trend away from the horizontal, and that the erratic departures are due to experimental errors. Additional evidence for this hypothesis may be obtained by considering measurements which were made for λ 4800 and 6800 A.U. on four different samples of Pyrex, over somewhat longer periods of time. The data are briefly summarized in table 1.

Samples AV and AVII were cut from one plate of Pyrex, which presumably differed in batch from the plate from which samples BI and BII were cut. The constancy of

$$\log \log (I_0/I)_{4800\text{ A.U.}} - \log \log (I_0/I)_{6800\text{ A.U.}}$$

for each series of measurements is demonstrated by the magnitude of the average departure from the average value, column three. That this quantity is also constant for the different samples of glass is evident from the data in column two. The last two columns are included to indicate the range of values covered.

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[3] It should be mentioned that this same relation may be based upon the assumption that any number of different colored substances are present, but that the ratios of their concentrations do not change with time or irradiation. The postulate implies also that the colored substance is distributed uniformly. This condition probably exists within the limits of sensitivity of our spectrophotometer. Moreover, it is not probable that the same surface of the glass was placed nearest the x-ray tube each of the many times it was returned for more irradiation. We intend to test in later experiments the distribution of colored material within the glass.

A series of measurements, similar to those summarized in figure 2, were made with a piece of flint glass, of unknown origin. The color distribution of this sample resembled that obtained for Pyrex within the limits of experimental error, and there is the same definite evidence that the ratio $a_\lambda/a_{\lambda,\text{reference}}$ is a constant. Qualitative experiments with "plate glass" and with Corex D indicated the same color distribution as was obtained for Pyrex.

TABLE 1

Evidence for the constancy of the quantity log $a_{4800A\ U.}$ — *log* $a_{6800A.U.}$

SAMPLE	LOG LOG $(I_0/I)_{4800A\ U.}$ −LOG LOG $(I_0/I)_{6800A\ U}$	AVERAGE ERROR OF THE AVERAGE VALUE	NUMBER OF MEASUREMENTS	DURATION OF EXPERIMENT IN HOURS
AV	0.63	0.02	21	110
AVII	0.63	0.01	11	310
BI	0.61	0.03	14	181
BII	0.67	0.02	16	186

RATE OF COLORING

The general form of the curve relating the absorption (for visible light) of glass to the duration of the exposure to x-rays has been established by the work of Kersten and Dwight (6). Quantitative interpretation of their results is difficult, since they measured the absorption of white light, and furthermore they used as their measuring instrument a photronic cell, the sensitivity of which is a function of wave length. In their experiments on the rate of fading of irradiated glass, they demonstrated that soft glass fades appreciably even at room temperature in the dark. This result was confirmed for samples of soft glass which were irradiated under our experimental conditions. However, the rate of fading of irradiated Pyrex proved to be much slower, amounting to not more than 2 or 3 per cent reduction in relative absorption[4] during a week at room temperature. For this reason, all of our experiments on rate of coloring were performed with samples of Pyrex.

In attempting to interpret our results, we have made the following assumptions. The rate at which the colored substance is formed is proportional to the product of the intensity of the absorbed x-rays and the concentration of some substance which reacts to form the colored material. Saturation is reached when this rate is counterbalanced by thermal fading and by a second process, which is proportional to the product of the intensity of the absorbed x-rays and the concentration of the colored substance. These assumptions may be expressed by the equation

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[4] That is from, say, 0.45 to 0.44.

$$\frac{dc}{dt} = k(M - C) - k'C - f(C, M, T) \tag{3}$$

where M is the initial concentration of the substance which can be transformed into the colored material, C is the concentration of the colored substance, t is time, T is temperature, and k and k' are factors which are directly proportional to the intensity of the absorbed x-rays. The term $f(C, M, T)$ represents the thermal rate of fading. In the following treatment, this last term (which is of unknown form) will be neglected, and the resulting equation will be applied to the experimental data for the first sixty hours of irradiation, during which time the rate of coloring (and therefore dc/dt) is relatively large compared to the thermal rate of fading.[5] With this term omitted, the equation may be written as

$$\frac{dc}{kM - (k + k')C} = dt \tag{4}$$

Integrating between the limits 0 and t and 0 and C,

$$C = \frac{kM}{k + k'}[1 - e^{-(k+k')t}] \tag{5}$$

Eliminating C between equations 1 and 5,

$$\log \frac{I_0}{I} = alM \frac{k}{k + k'}[1 - e^{-(k+k')t}] \tag{6}$$

$$= \alpha(1 - e^{-\beta t}) \tag{7}$$

where α is a positive coefficient, which is directly proportional to the thickness of the glass (l) and the absorption coefficient (a) for the analyzing light, but is independent of the intensity of the absorbed x-rays, and β is a positive exponent which is directly proportional to the intensity of the absorbed x-rays.

It is interesting to note that equation 7 is consistent with two widely different hypotheses. Either that the initial concentration M is extremely small and that saturation is reached when this substance is used up, no radiochemical back reaction being assumed; or that the initial concentration M is large enough so that the concentration $M - C$ is not sensibly altered by irradiation, and that saturation is a steady state at which the radiochemical forward and back reactions are equal.

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[5] Glass samples which were irradiated for two or three hundred hours did not gradually approach a constant saturation value (as was expected), but showed an erratic fluctuation, of from 5 to 10 per cent of the relative absorption, around this constant value. This fluctuation was probably the result of our experimental technique, being due chiefly to changes in the room temperature and to changes in the intervals which elapsed between irradiation periods. We are planning to repeat this work under conditions which will minimize these factors.

Equation 7 was tested by fitting it (graphically) to the experimental data. The curves in figures 3, 4, and 5 are plots of the equation. The corresponding experimental points are represented by circles. The values used for the constants α and β are summarized in table 2. The first two columns of this table refer to the numbers of the figures and of the glass samples. The wave length of the analyzing light is given in column three, and the thickness of the glass in column four. The values of the constants are given in the last two columns; of these, the four values printed in heavy type were determined empirically. The constants of the equation were first determined to fit the data for sample BIII, figure 3. The same value for β was used for all experiments, except those on sample BI. For all data obtained with λ4800 A.U. as the analyzing light, the value of α used was $0.81 \times l/3.94$ mm. To allow for the difference in the absorption coefficient (a), the values of α for experiments with λ6800 A.U. were obtained by multiplying the corresponding value (i.e., for the same sample and irradiation) for λ4800 A.U. by the empirical factor 0.25. The value of β was determined empirically from the data for B1, λ4800 A.U., since this sample was not exposed directly to the x-rays, but was surrounded by a copper filter which decreased the intensity and increased the average requency of the absorbed x-rays.

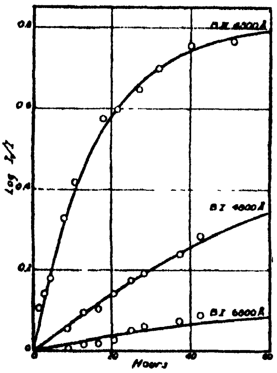

FIG. 3
RATE OF COLORING

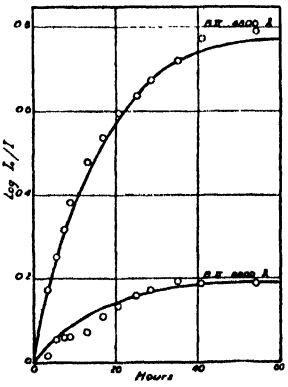

FIG. 4
RATE OF COLORING

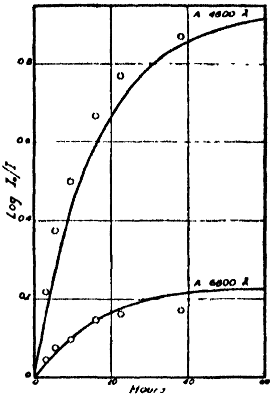

FIG. 5
RATE OF COLORING

The graphs demonstrate that, with the exception of the data for sample

A, figure 5, the experimental points are fitted by equation 7 within the limits of experimental accuracy. The curve for sample A is uniformly about 10 per cent lower than the experimental points. However, it must be remembered that samples A and B were not taken from the same lot of Pyrex, and there is no *a priori* reason for assuming (as we have) that the values of α and β will be the same for different batches of Pyrex. If the initial concentration M were 10 per cent greater in sample A than in sample B, the discrepancy would be explained.[6]

Since we have assumed that k and k' are directly proportional to the intensities of the absorbed x-rays, we should expect that the ratio of the values of β, for the experiments with filtered and unfiltered x-rays, would be equal to the ratio of the energies absorbed from the x-rays. The ratio of the values of β is $0.064/0.0096 = 6.7$; the experimentally determined ratio of the intensities of the absorbed x-rays is 8.3. While these ratios are substantially in agreement, their difference is probably larger than the experimental error. The difference may be ascribed either to a departure from direct proportionality between k_2 (and possibly k_1) and the intensity, or to a relatively greater efficiency of the more penetrating x-rays transmitted by the copper filter.

TABLE 2

Summary of data of figures 3, 4, and 5. A test of equation 7

FIGURE	SAMPLE	λ	l	α	β
		A.U	*mm.*		
3	BIII	4800	3 94	**0.81**	**0.064**
4	BII	4800	3 85	$0.79 = \frac{3\ 85}{3.94}\,0.81$	0.064
5	A	4800	4 54	$0.93 = \frac{4\ 54}{3\ 94}\,0\ 81$	0.064
4	BII	6800	3 85	$0.20 = \mathbf{0.25} \times 0.79$	0.064
5	A	6800	4 54	$0.23 = 0\ 25 \times 0.93$	0.064
3	BI	4800	3 85	$0.79 = \frac{3\ 85}{3.94}\,0\ 81$	**0.0096**
3	BI	6800	3 85	$0.20 = 0.25 \times 0.79$	0.0096

The coloring due to α-, β-, and γ-rays

The effect of x-rays on glass is, in many respects, similar to the effects of the radiations from radioactive substances. The distribution of absorption, as a function of the wave length of the analyzing light, seems to be quite independent of the type of radiation. The color of glass irradiated by hard x-rays appears to be quite homogeneous, but glass which is exposed to the complete radiation from radon or radium salts develops three layers of differing intensity. α-Rays produce a thin skin of intense color, about 0.04 mm. thick (10). β-Rays produce a layer of intermediate intensity, which shades off gradually but appears to be about 2.5 mm. thick (2). The energy absorbed from the accompanying γ-rays is very much smaller, and the coloring of glass by them is correspondingly slow, but is of course uniform. Some measurements made on the coloring of the plane ends (3.4 mm. thick) of a cylindrical Pyrex cell, of 30 cc. volume, which was filled with about 100 millicuries of radon, may be of interest in this connection. The color increased very rapidly at first, and appeared to a casual inspection to have reached saturation after forty-eight hours. However, sensitive photometric measurements revealed that the color was still increasing slowly after three hundred hours had elapsed. A second and even a third charge of radon (of approximately 100 millicuries each) failed to bring the color to a saturation value. In our opinion, these facts indicate that a source which produces either α- or β-rays is not well adapted to quantitative measurements on the coloration of glass. On the other hand, a pure γ-ray source is (except for the inconvenient slowness of its action) an ideal one for the purpose.

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[6] This assumption is consistent with the first hypothesis, that M is very small, being the concentration of some impurity.

Experiments on the rate of coloring of glass subjected to the complete radiation from radium sulfate have been reported by Kabakjian (5). His absorption measurements appear to have been made with white light. The equation which he develops to fit the data is based upon the assumption that saturation is reached when the rate of thermal fading is equal to the rate of coloring due to the absorbed radiation. As the author points out, the known extremely slow rate of thermal fading (at room temperature) and certain inconsistencies in the empirically determined values of the constants make it practically certain that the agreement between the experiments and the equation is fortuitous.

An equation similar to that derived in this paper was presented in 1923 by Belar (1) to represent the rate of coloration of rock salt subjected to β- and γ-radiation. In 1926, Przibram (8) subjected the question to a thorough analysis and decided that the formula of Belar was not sufficient to represent all of the facts; he derived a more complex expression which was consistent with the available data on the coloring of rock salt by β- and γ-radiation. In these experiments it was established that the saturation value of the absorption is a function of the intensity of the absorbed β, γ-radiation. Kabakjian's claim that the saturation limit is a function of intensity for glass irradiated by α, β, γ-radiation does not appear to be definitely proven. There is at present no evidence to indicate that a similar effect exists in the coloring of glass by x-rays. Further experiments should be performed, using hard x-rays or γ-rays under carefully controlled conditions to test this point and to throw some light on the various questions raised by the present work.

SUMMARY

Some experiments have been performed on the rate of coloring of Pyrex glass by irradiation with hard x-rays, and on the distribution of relative absorption, of the colored glass, as a function of wave length for visible light. A simple hypothesis of the rate of coloring has been suggested, an equation has been derived from this hypothesis, and it has been shown that the experimental measurements are in agreement with the equation. Some discussion of the analogous effects of radiations from radium is included.

In conclusion we wish to express our appreciation of the coöperation and interest of Dr. Wilhelm Stenstrom, of the Cancer Institute, and of Prof. S. C. Lind, Director of the School of Chemistry.

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THE PHYSICAL CHEMISTRY OF FLOTATION. VI

THE ADSORPTION OF AMINES BY SULFIDE MINERALS

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Wark and Wark (4) have used the measurement of contact angle at the line of triple contact air–solid–water as a means of studying adsorption by the solid of the class of compounds known in flotation as "collectors." It was shown that, for a group of soluble collectors containing the —SH group or its alkali metal salts, the angle of contact is dependent only upon the specific non-polar group of the adsorbed collector. Though the collectors most commonly used today for the flotation of the sulfide minerals are almost all of this type, several other types are of considerable theoretical interest, namely: (1) soluble salts of the fatty acids, in which, as in the xanthate type, the non-polar group is in the negative ion; (2) soluble salts of the amines, in which the non-polar group is in the positive ion; (3) sparingly soluble oils. The first of these types is being investigated elsewhere by the contact angle method. Work on the second type is described in this paper. Work on the third type is to be undertaken shortly.

Amines have been chosen to facilitate a comparison between (a) different members of the series of primary amines from the methyl to the hexyl derivatives, (b) different members of the series of quaternary amines from the methyl to the amyl derivatives, (c) the ethyl derivatives of the primary, secondary, tertiary, and quaternary series, and (d) the aliphatic and the aromatic amines.

EXPERIMENTAL METHOD

Preparation of amines

The primary, secondary, and tertiary amines were recrystallized as the hydrochlorides, usually from alcohol, by addition of ether. The quaternary ammonium salts were recrystallized from water.

Determination of contact angle

The experimental procedure of the preceding papers was followed, but in the present work higher concentrations of the collector were generally necessary to induce contact. Since limited amounts of the amines were available, the response of the minerals could not be tested in solutions of greater concentration than 1 g. per liter. In every test, the reaction of the mineral to the amine was observed over a period of at least half an hour, and the bubble was pressed against the mineral for approximately fifteen seconds to see whether true contact was established.

The pH value of the solution was found to influence the adsorption of amines. Consequently, if a mineral failed to respond to the natural solution of the amine hydrochloride, its behavior was observed also in acid (pH = 1) and alkaline (pH = 12) solutions. Even with this procedure, adsorption of isoamylamine by sphalerite was not detected. Gaudin, Haynes, and Haas (1) have shown that flotation in this case occurs only within the pH range 9 to 11. It is possible, therefore, that in a few cases contact angles are reported as "nil" where tests at other pH values would have shown contact to be possible.

RESULTS

No matter what the concentration of an amine may be, a characteristic contact angle is never exceeded. Near the minimum effective or "threshold" concentration of amine, or near the critical pH value—at which contact ceases to be possible—there is a range of solution compositions over which the maximum contact angle is not attained. However, over a wide range of concentrations and of pH values, the contact angle is constant within an experimental error of ±2°. The determined *maximum* contact angles are recorded in table 1. Over a wider range of pH values than other minerals, bornite and chalcocite do not give the usual maximum angles for the aliphatic amines. On the other hand, both these minerals adsorb sulfur-bearing collectors more readily than does chalcopyrite, and the incomplete response to amines may be due to fouling of the surface by cuprous chloride or iodide. Certainly both minerals float readily with hexylamine under solution conditions that lead to angles of contact of only 40° to 50°, the amine itself serving as frother. With triethylamine, however, for which the measured contact angles were still lower, only a very rapidly collapsing mineralized froth could be obtained, even in the presence of an added frother.

When placed in amine-free distilled water, a chalcopyrite surface that has previously responded to hexylamine or to a quaternary ammonium salt retains for some time the ability to attract an air bubble. It is evident, therefore, that the amine changes the surface of the mineral. The change, attributed to adsorption of the amine, is most permanent for those amines that are most readily adsorbed.

Methylamines. Trimethylamine hydrochloride and tetramethylammonium iodide were tested. Within the pH range considered, none of the minerals with which the investigation was concerned would have responded to a 1 g. per liter solution of the primary or secondary methylamines.

None of the minerals responds to a concentration of 1 g. per liter of trimethylamine hydrochloride at pH values of 7 or 12. To a solution of 1 g. per liter at a pH value of 1.0, only chalcopyrite and bornite responded, and then but weakly; in normal hydrochloric acid, however, the response of chalcopyrite to the amine was complete. Sphalerite that had been previously activated[1] responded in acid solution in a manner similar to chalcopyrite.

TABLE 1

Maximum values of contact angle for various minerals and amines

AMINE	MAXIMUM VALUES OF CONTACT ANGLES FOR VARIOUS MINERALS						
	Chalcopyrite $CuFeS_2$	Sphalerite, ZnS	Sphalerite activated by $CuSO_4$	Bornite, Cu_3FeS_3	Chalcocite, Cu_2S	Pyrite, FeS_2	Galena, PbS
Trimethylamine hydrochloride	61*	Nil	59*	(49)*	Nil	Nil	Nil
Monoethylamine hydrochloride	58*	Nil	Nil	(42)*	Nil	Nil	Nil
Diethylamine hydrochloride	61*	Nil	Nil	(44)*	Nil	Nil	Nil
Triethylamine hydrochloride	61	Nil	63	(52)*	Slight	Nil	Nil
Isoamylamine hydrochloride	63	Nil	60	(52)	Slight*	Nil	Nil
Isohexylamine hydrochloride	63	61	56	(47) 64†	(49) 62†	63	Nil
Aniline hydrochloride	56	Nil	57	59	57	Nil	Nil
α-Naphthylamine hydrochloride	62	(55)*	62	Slight Slight†	59	Nil	Nil
Piperidine hydrochloride	61	Nil	58*	56	Slight*	Nil	Nil
Tribenzylamine hydrochloride‡	61	Nil	62	62	(56)	Nil	60
Tetramethylammonium iodide	60	Nil	61	61	(50)	Nil	Nil
Tetraethylammonium iodide	61	Nil	61	60	61	Nil	(54)*
Tetrapropylammonium iodide	61	Nil	60	56	(52)	Nil	(52)
Tetrabutylammonium iodide	62	60	59	61	61	Nil	62
Tetraamylammonium iodide	59	60	57	60	60	Nil	62

* At pH = 1.0.

† At pH = 12.0.

‡ Maximum pH value 3.5.

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[1] Sphalerite that has been immersed in a dilute copper sulfate solution becomes coated by a copper-bearing film, probably of cupric sulfide. When in this condition, it responds more readily to most collectors, and is regarded as being "activated."

The copper minerals respond to 1 g. per liter of tetramethylammonium iodide, but neither galena, sphalerite, nor pyrite responds within the pH range 1 to 12. Chalcopyrite, however, responds to so low a concentration as 25 mg. per liter, and the response of bornite, chalcocite, and sphalerite activated by copper sulfate, to neutral 1 g. per liter solutions is rapid. The contact angle for chalcocite (see table 1) was influenced by the formation of a heavy precipitate, presumably of cuprous iodide. In neutral solution, the angle of contact for bornite was 61°, but contact was slower and less complete (= 50°) at pH = 12.

Ethylamines. The mono-, di-, tri-, and tetra-substituted ammonium salts indicate a slight increase in the readiness with which adsorption occurs as the number of non-polar groups in the adsorbed molecule increases. Solutions of a constant concentration (1 g. per liter) were used for all four amines. The differences between them would have been slightly greater had equivalent concentrations been taken.

Monoethylamine is a slightly less potent collector than trimethylamine. None of the minerals responds to 1 g. per liter of ethylamine hydrochloride in neutral or alkaline solutions (pH = 12) and only chalcopyrite responds completely in an acid solution of pH value = 1. Bornite gives an angle of approximately 40° at pH = 1, the response being irregular over the surface.

Diethylamine hydrochloride was adsorbed only by those minerals that adsorbed the primary amine. Again, none of the minerals responds to 1 g. per liter in neutral solution or at pH = 12, and only chalcopyrite and bornite respond in acid solution. The response of bornite is again incomplete.

With triethylamine the response of the minerals is slightly more general. Pyrite, sphalerite, and galena, however, fail to respond to 1 g. per liter of the hydrochloride over the whole pH range 1 to 12. Activated sphalerite does respond, particularly in acid solution. Chalcocite responds incompletely, the angle of contact being only 38° at pH = 1, and it does not respond in alkaline solution. Though bornite responds over the whole pH range, the contact angle is low, a maximum angle of 51° being obtained at pH = 1. Chalcopyrite responds rapidly to the neutral solution.

The quaternary ammonium salt is more effective than triethylamine as a collector. The copper minerals and activated sphalerite respond rapidly to a 1 g. per liter solution of tetraethylammonium iodide in neutral solution; indeed, much lower concentrations than 1 g. per liter may be used. Galena responds in a strongly acid solution (pH = 1), but the full contact angle is not attained. Neither pyrite nor sphalerite responds to a 1 g. per liter solution within the pH range 1 to 12.

Isoamylamine. Though more effective as a collector than monoethylamine, isoamylamine is no more effective than triethylamine. Galena and pyrite do not respond to a 1 g. per liter solution of isoamylamine hydrochloride at pH values 1, 6, and 12. However, sphalerite, which does not respond at pH values of 6 and 12, does respond at 10. The copper minerals and activated sphalerite respond to a 1 g. per liter solution at the natural pH value (3.8). Chalcopyrite responds to very low concentrations in acid solution (see figure 2).

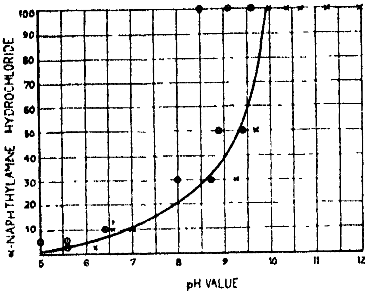

FIG. 1

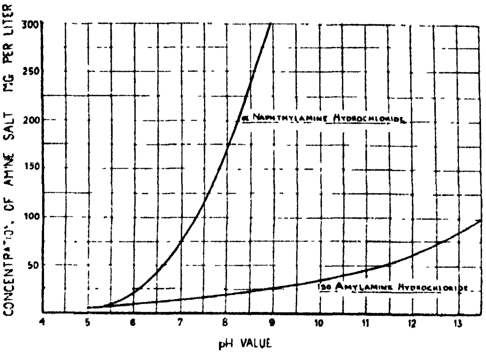

FIG. 2

FIG. 1. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF α-NAPHTHYLAMINE HYDROCHLORIDE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND A CHALCOPYRITE SURFACE

⊙, contact possible; X contact impossible. Contact possible only to left of curve.

FIG. 2. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF AMINE HYDROCHLORIDE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND A SURFACE OF CHALCOPYRITE

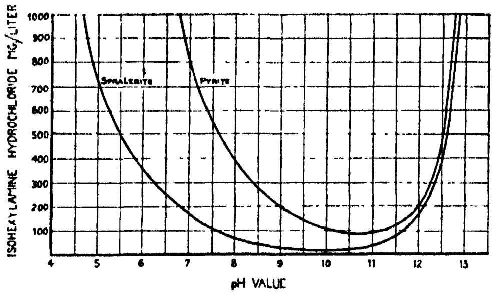

FIG. 3. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF ISOHEXYLAMINE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND SURFACES OF SPHALERITE AND PYRITE

Contact possible only above curves

Isohexylamine. Isohexylamine is a still more effective collector than the corresponding amylamine. It is a good collector for sphalerite, the optimum pH value being about 10 (see figure 3). Even pyrite responds to sufficiently concentrated solutions of the hydrochloride over a limited pH range. Galena alone fails to respond at the pH values tested.

Aniline. As a collector, aniline resembles isoamylamine. Sphalerite, galena, and pyrite do not respond to a 1 g. per liter solution of aniline hydrochloride within the pH range tested, but the copper minerals and activated sphalerite do respond to a solution at the natural pH value of 3.5.

α-Naphthylamine. α-Naphthylamine is a little more effective than aniline; sphalerite responds slowly and incompletely to 1 g. per liter of the hydrochloride in acid solutions. However, neither galena nor pyrite responds to it. Accordingly, sphalerite can be floated away from galena by a 1 g. per liter solution of the amine hydrochloride at a pH value of 3.5. The amine itself serves as a frother.

Piperidine. Piperidine and α-naphthylamine are of approximately equal value as collectors, the former being slightly the more active.

Tribenzylamine. The solubility of tribenzylamine hydrochloride in water is less than 200 mg. per liter; a saturated solution was therefore employed. Since alkalis precipitate the amine from this solution, no tests could be made in alkaline solution. Only the natural solution (pH = 3.5) and a solution of pH value = 1 were tested. This amine is the strongest collector of the aromatic derivatives tested. Even with this low concentration, only sphalerite and pyrite failed to respond to it in acid solutions.

Tetrapropylammonium iodide. Of the minerals tested, only pyrite and sphalerite do not respond to 1 g. per liter of this reagent within the pH range 1 to 2. The response of chalcocite is masked by the formation of a precipitate of cuprous iodide, and though galena responds to a neutral 1 g. per liter solution, its response is not fully developed. The copper minerals respond in the natural solution (pH = 6.6) to considerably less than this concentration of the amine; indeed, chalcopyrite responds fully to 25 mg. per liter.

Tetrabutylammonium iodide. With the increase in the size of the nonpolar portions of the amine, adsorption becomes still more general, and sphalerite responds to this collector without the need for activation. Pyrite, however, remains uninfluenced by 1 g. per liter of the reagent over the pH range 1 to 12. Concentrations as low as 25 mg. per liter are effective for the copper minerals and activated sphalerite.

Tetraamylammonium iodide. Of the minerals tested, pyrite alone does not respond to a 1 g. per liter solution of tetraamylammonium iodide within the pH range 1 to 12. The other minerals respond to considerably lower concentrations.

INFLUENCE OF pH VALUE

In general, the amines are more readily adsorbed from acid than from alkaline solutions. However, in two cases at least—namely, for sphalerite and pyrite with hexylamine—adsorption ceases to be possible in acid solutions, and in fact takes place more readily from alkaline solutions. In these cases, there is an optimum pH value between 9 and 11 *for contact* between air and mineral; Gaudin, Haynes, and Haas (1) give an optimum pH value of about 10 *for flotation* of sphalerite by isoamylamine. The copper minerals exhibit no such optimum pH value within the range tested (3.4 to 13). With them there is, for each pH value, a concentration of collector above which contact is possible between mineral and air and below which contact is impossible. This concentration is dependent both on the mineral and on the amine.

Curves have therefore been determined to show the influence of pH value on the threshold concentration of the amine for a number of minerals and amines. The method of determining the curves is best illustrated by figure 1, which shows for chalcocite the relationship between pH value and concentration of α-naphthylamine hydrochloride. The response of chalcocite to a number of solutions of differing concentration and pH value was determined. The compositions of solutions in which contact with an air bubble was possible appear on the diagram as circles; those of solutions in which contact was not possible appear as crosses. Where the response over the surface was irregular, or where the contact angle fell short of 60°, the solution composition appears on the diagram as a crossed circle. A smoothed line is then drawn between the two sets of points; obviously it separates solutions in which contact is possible from those in which contact is not possible. Fuller details of the method are given elsewhere (2). In general, the curves for amines cannot be determined with the same precision as those for xanthate, the range of incomplete contact being bigger. In figure 2 are shown the curves for chalcopyrite with two different amines, and in figure 3, the curves for sphalerite and pyrite with isohexylamine.

DISCUSSION OF RESULTS

The maximum angles of contact cited in table 1 are approximately constant for all the amines tested; the mean value is 60° and the variation therefrom is usually within the experimental error. This angle is independent both of the nature of the mineral and of the concentration of the collector, provided that the latter exceeds a "threshold concentration" characteristic of the mineral, the amine, and the pH value of the solution. The threshold concentration is lowest for the copper minerals, and then follow, in order of their susceptibility to the quaternary ammonium salts, galena, sphalerite, and pyrite. Sphalerite preactivated by copper sulfate closely resembles chalcopyrite in its response to amines; this is in accord with its response to the sulfur-bearing collectors.

Though galena responds more readily than sphalerite to the quaternary amines, sphalerite responds more readily to hexylamine. Using 50 mg.

per liter of hexylamine at a pH value of 10.5, sphalerite can be floated away from galena. The amine serves both as collector and frother. With collectors of the xanthate type, galena can be floated away from sphalerite; in this case a frother is necessary. It follows that the function of the collector in selective flotation is not merely to enhance differences in the inherent floatability of the minerals to be separated, as has been suggested by some writers, but actually to alter the surface of the desired mineral so that it can be floated.

Of the amines tested, the quaternary ammonium salts are the most readily adsorbed. Further, the higher the homolog the lower is the concentration necessary for the mineral to respond. For example, considering the ethylamines, the primary compound induces a marked response only in one mineral, chalcopyrite, and then only in strongly acid solutions; the secondary compound is little if any more active; the tertiary compound is, however, very much more active, though it does not influence pyrite or galena, and only slowly influences sphalerite in acid solutions; while the quaternary compound induces a response from all the minerals except pyrite and sphalerite. Similarly, tetraamylammonium iodide is very much more active than primary amylamine.

Among the primary amines the higher members of the series are far more active than the methyl and ethyl compounds. Three of the four aromatic amines considered are of about the same order of activity as isoamylamine, but tribenzylamine is more active.

An analysis of the influence of acids and alkalis suggests that in general the amine may be adsorbed in the form of an ion, e.g. $(N(Et)_4)^+$, $(N(Et)_3H)^+$, $(NEt_2H_2)^+$, $(NEtH_3)^+$, etc. The greater the hydrogen-ion concentration the greater will be the percentage of the amine present in the ionic form (and the less in the form of the amine itself or of the hydroxide) and consequently a smaller addition of amine would produce the threshold concentration of the amine ion necessary for adsorption.

The loss of floatability with decrease of pH value for sphalerite and pyrite in the presence of hexylamine cannot be explained in this manner. There, up to a certain point, an increase in alkalinity permits of a smaller addition of amine; thereafter (figure 3), the curves are of the normal form. No explanation is offered for the increase in concentration shown on the left of these two curves. Gaudin, Haynes, and Haas have shown (1) that the relationship between flotation and pH value may be very complex.

The approximate constancy of the angle of contact for all the amines tested indicates that the forces responsible for the adsorption of the amines differ from those responsible for the adsorption of the soluble collectors of the xanthate type. This is perhaps due to the fact that the non-polar groups are in the positive ion in amines and in the negative ion in xanthates.

If, as has been suggested (3), ionic forces bind the xanthate ion to the surface, the forces of adsorption *must* be of a different nature in the two cases.

Using sphalerite and hexylamine, it has been possible, for the first time, to determine experimentally how closely contact angle tests parallel actual flotation tests carried out in identical solutions. Concentrations of this amine that are sufficient to cause contact between air and mineral are also sufficient to produce frothing. Moreover, the amount of the amine abstracted by the mineral is low and the concentration of the amine in solution can therefore be calculated approximately from the amount added.

By means of flotation tests carried out in test tubes (3) a curve can be constructed showing the relationship between the pH value and the amount of amine necessary to induce flotation. Such a curve approximately coincides with the corresponding contact curve of figure 3, but there is not absolute agreement between them. In comparing flotation tests with the contact curve, it was found that, keeping the amine concentration constant at 1 g. per liter, flotation of sphalerite is impossible at pH values below 5; that at a pH value of between 5.5 and 6 an ephemeral mineralized froth forms; that when the pH value is increased to 8, flotation becomes stable; but that at a pH value of 13 only the very fine material floats.

Keeping the pH value constant and gradually increasing the concentration of the amine it was found that: (a) with the pH value at 9.5, no flotation occurs with 15 mg. per liter, only an ephemeral mineralized froth forms at 25 mg. per liter, and a permanent mineralized froth forms at 50 mg. per liter; (b) with the pH value at 6.6, no flotation occurs at 100 mg. per liter or 200 mg. per liter, slight flotation occurred at 250 mg. per liter, and good flotation occured at 300 mg. per liter; (c) with the pH value at 13, good flotation occurred at 2 g. per liter. Except in the last-mentioned case these results are in agreement with the contact curve.

A similar comparison has been made for chalcopyrite and α-naphthylamine (compare figure 2). With a concentration of 500 mg. per liter in strongly acid solutions no froth is produced, but the mineral gives good film flotation. As alkali is added the solution acquires the capacity to form a froth, and between pH values of 6 and 9 a stable mineralized froth is produced. Beyond pH = 10, although the frothing power increases, flotation falls away, until at pH = 12 no permanent mineralized froth can be formed. At lower concentrations an additional frother is necessary, and the comparison loses significance.

SUMMARY

1. Table 1 shows that the maximum contact angle is independent of the particular amine chosen, being within a few degrees of 60° for all amines.

2. The amine induces a more or less permanent effect on the mineral surface, and it is concluded that adsorption of the amine is responsible for this.

3. Of the minerals tested, the copper minerals respond most readily, and pyrite least readily, to amines; activated sphalerite closely resembles chalcopyrite in its response.

4. Using hexylamine, sphalerite can be floated away from galena.

5. Of the amines tested, the quaternary ammonium salts are most readily adsorbed.

6. The higher the homolog, the lower is the concentration necessary for the mineral to respond, i.e., the ethylamines are more effective than the methylamines, the propylamines than the ethylamines, etc.

7. The primary amines are the least active, the secondary amines are more active, and the tertiary amines are still more active.

8. Three cyclic amines—aniline, α-naphthylamine, and piperidine are of about the same order of activity as isoamylamine, but tribenzylamine is much more active.

9. Contact tests closely parallel actual flotation tests carried out in identical solutions.

10. Figures 1, 2, and 3 show how the contact induced at certain mineral surfaces by certain amines is prevented by addition of alkali or acid.

We wish to record our thanks to Professor E. J. Hartung for having made available a laboratory for this work, and to Messrs. H. Hey and A. B. Cox for help during its progress. The cost of the work was borne by the University of Melbourne and the following Companies: Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Company of Australasia Ltd., Mount Lyell Mining and Railway Company Ltd., and the Burma Corporation Ltd.

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THE APPARENT VOLUMES AND APPARENT COMPRESSIBILITIES OF SOLUTES IN SOLUTION. II

CONCENTRATED SOLUTIONS OF LITHIUM CHLORIDE AND BROMIDE

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In the first paper (11) of this series it was shown that, from the standpoint of the apparent molal volume and compressibility, concentrated solutions of lithium chloride and bromide differ significantly from solutions of other strong electrolytes. It was impossible, however, with the limited data at hand to determine at what concentration these solutions become abnormal or to study the nature of the irregularity. The object of this paper is to report new measurements of the density and compressibility coefficient of concentrated solutions of these salts and to present a more complete picture of the anomalous properties of these solutes.

The results of seven new experiments are summarized in table 1. No detailed description of these experiments will be given here, because the procedure followed throughout was the same as that described fully in a previous communication (10). It should be noted, however, that new stock solutions of both lithium chloride and lithium bromide were prepared for these experiments, and that all other solutions investigated were prepared by dilution of weighed portions of these stock solutions.

From these data have been calculated the apparent molal volume ϕ, the apparent molal compressibility $(\bar{B} + f)$, and the volume concentration of the solute in the several solutions. Values of these calculated quantities are given in table 2, which may be regarded as a supplement to table 2 given in paper I. With the exception of some of the f values, the method of calculating these quantities is the same as that already described (11). The modification in the method for calculating f may be outlined briefly. It will be recalled that by definition

$$\phi = V - n_1 V_1$$

and

$$\bar{B} = \frac{-\mathrm{d}\phi}{\mathrm{d}P} = V\beta - n_1 V_1 \beta_1$$

where V = volume of solution containing 1 gram-mole of solute,
V_1 = volume of 1 gram-mole of pure water at the temperature of the solution,
n_1 = number of moles of water present in the solution, and
β, β_1 = compressibility coefficients of solution and water, respectively.

ϕ, however, is a function of two independent variables, pressure and concentration,

$$\phi = F(P, c)$$

and we can write for the total differential

$$\mathrm{d}\phi = \left(\frac{\partial \phi}{\partial P}\right)_c \mathrm{d}P + \left(\frac{\partial \phi}{\partial c}\right)_P \mathrm{d}c$$

Dividing through by $\mathrm{d}P$, we get

$$-\bar{B} = \frac{\mathrm{d}\phi}{\mathrm{d}P} = \left(\frac{\partial \phi}{\partial P}\right)_c + \left(\frac{\partial \phi}{\partial c}\right)_P \frac{\mathrm{d}c}{\mathrm{d}P}$$

The quantity f is the last term of this expression

$$f \equiv \left(\frac{\partial \phi}{\partial c}\right)_P \frac{\mathrm{d}c}{\mathrm{d}P}$$

whence

$$\bar{B} + f = -\left(\frac{\partial \phi}{\partial P}\right)_c$$

The method of calculating f, given in paper I, was for the special case where ϕ is a linear function of $c^{\frac{1}{2}}$ at constant pressure (Masson's rule). For the concentrated solutions of the lithium halides where this relationship is not valid, it has been necessary to proceed as follows. The numerical value of the slope $\frac{\partial \phi}{\partial c}$ was found graphically from a plot of ϕ against c. Further, since

$$c = 1000/V$$

it follows that

$$\frac{\mathrm{d}c}{\mathrm{d}P} = \frac{-1000}{V^2}\frac{\mathrm{d}V}{\mathrm{d}P} = \frac{1000}{V}\beta = c\beta$$

The product $c\beta$ affords a simple means of getting the numerical value of the second term necessary for the evaluation of f. It should perhaps be noted here again that the calculated values of $\bar{B}$ derived from our data refer to solutions under a pressure of 200 metric atmospheres, and that therefore the f values must be calculated for the same condition. This requirement was met in the calculation of the f values given in table 2.

The graphical method of computing f just described has also been applied to the calculation of the f values omitted from table 1 of the first paper (11). For the sake of completeness these new values as well as some recalculated ones are included in table 3. For purpose of identification only the $\bar{B}$ values given in the table referred to are repeated here.

TABLE 1

Table of results

SOLUTION NO.	WEIGHT PER CENT OF SALT	DENSITY AT 35°C	$\beta \times 10^6$	AVERAGE DEVIATION
Lithium chloride solutions				
1	41.020	1.25597	20.44	0.01
2	37.003	1.22536	21.86	<0.01
3	27.450	1.15772	25.62	<0.01
Lithium bromide solutions				
1	45.183	1.44911	27.12	
2	39.999	1.37671	28.63	<0.01
3	34.706	1.31036	30.11	<0.01
4	18.076	1.13859	35.28	

TABLE 2

Values of the various solution factors at 35°C.

SOLUTION NO	c	c_{200}	ϕ	ϕ_{200}	$-\bar{B} \times 10^4$	$f \times 10^4$
Lithium chloride solutions						
1	12.152	12.201	20.97	21.14	8.82	0.11
2	10.695	10.734	20.89	21.08	9.91	0.11
3	7.496	7.534	20.68	20.95	12.94	0.09
Lithium bromide solutions						
1	7.5385	7.5793	26.64	26.82	8.31	−0.05
2	6.3400	6.3762	26.66	26.85	9.60	−0.12
3	5.2359	5.2675	26.61	26.83	10.94	0.16
4	2.3696	2.3863	26.02	26.35	16.57	0.25

The relationships existing between the apparent properties and concentration in solutions of these lithium salts are portrayed in figures 1 and 2, which were constructed by plotting the values of ϕ_{200} (left-hand scale) and ($\bar{B} + f$) values (right-hand scale), against the corresponding c_{200} values. The plotted values are those given in tables 2 and 3 of this paper and table

1 of paper I. Quantities for solutions under a pressure of 200 metric atmospheres have been used as in paper I in order to have them under the same conditions with the least loss in the precision of the original measurements. To show the molecular composition of the more concentrated solutions another scale is given at the top of each graph, which indicates the number of moles of water, n_w, per mole of solute in the solution, the concentration of which is given below on the abscissa scale.

TABLE 3

Values of f by graphical method

Lithium chloride solutions

$-B \times 10^4$ . .	8.83	10.55	13.90	14.91	17.34	18.62	22.69	27.09
$f \times 10^4$ . .	0.11	0.11	0.23	0.24	0.29	0.33	0.34	0.26

Lithium bromide solutions

$-B \times 10^4$ . .	5.25	6.38	7.27	8.22	8.62	10.74	12.05	14.13	17.20	17.58	20.00
$f \times 10^4$	−0.15	−0.27	−0.32	−0.05	−0.07	0.16	0.16	0.16	0.24	0.21	0.18

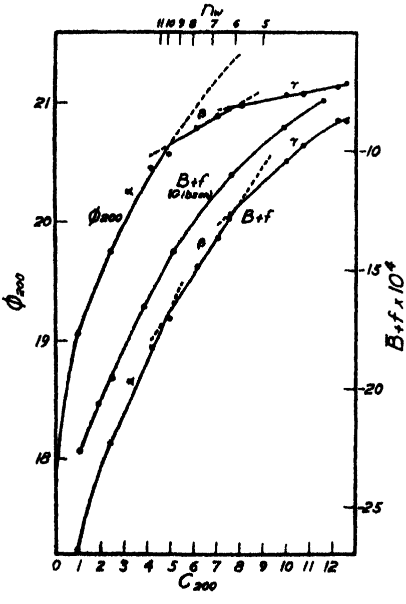

Fig. 1

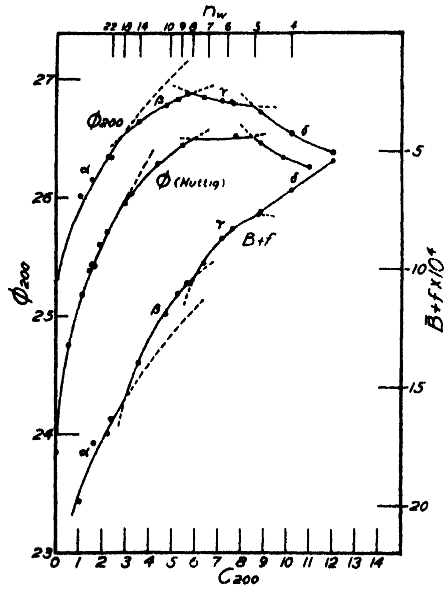

Fig. 2

Fig. 1. Apparent Molal Volumes and Apparent Molal Compressibilities of Lithium Chloride Plotted against Concentration

Fig. 2. Apparent Molal Volumes and Apparent Molal Compressibilities of Lithium Bromide Plotted against Concentration

On the basis of several recent studies (3, 6, 7) of the question it may be stated that the variation of ϕ with c in solutions of strong electrolytes is represented satisfactorily by the Masson equation:

$$\phi = kc^{\frac{1}{2}} + \phi^0$$

where k and ϕ^0 are constants dependent on temperature and pressure. From the Masson relationship a similar expression can be deduced for the relationship between $(\bar{B} + f)$ and c:

$$(\bar{B} + f) = -\frac{\partial k}{\partial P} c^{\frac{1}{2}} + \bar{B}^0$$

These normal relationships have been shown (11) to be valid for dilute solutions of lithium halides and are depicted in the graphs by the curves marked α. The numerical values of the constants of the above equations which were used in computing the α curves were estimated from the figures given by Geffcken (3) for solutions at atmospheric pressure and from the additive relationships found in paper I. The values of these constants are:

SALT	k_{200}	ϕ^0_{200}	$-\left(\frac{\partial k}{\partial P}\right)_{200} \times 10^4$	$\bar{B}^0_{200} \times 10^4$
LiCl	1.28	17.75	8.05	−34.90
LiBr	1.05	24.71	5.99	−26.00

An inspection of the graphs shows clearly that the simple square-root relationship (α curves) is not valid in concentrated solutions. Since our present interest is a detailed description of these irregularities, we shall examine the chloride and bromide graphs separately.

The ϕ–c plot for solutions of lithium chloride gives evidence of three distinct relationships between ϕ and c, depending on the concentration range: α (normal), β, and γ. The critical concentrations which mark the limits of these relationships, that is, the concentrations at which discontinuities in the ϕ–c plot occur, correspond, so far as can be ascertained, to solutions containing an integral number of moles of water per mole of solute. Thus reading from the graph we get:

Intersection of curves	*Values of n_w*
α–β	10
β–γ	6

The critical $n_w = 10$ value is the same as that which Masson (6) showed to be the limit of validity of his relationship at 18°C. and atmospheric pressure. The second critical value has not been reported before. As might be anticipated, discontinuities in the $(\bar{B} + f)$–c plot occur at the same critical concentrations, but they are less marked than in the ϕ–c plot. For the sake of comparison we have included in the graph another plot of $(\bar{B} + f)$ values derived from the recent measurements by Gibson (2). These values of $(\bar{B} + f)$ are for solutions under a mean pressure of 500 atmospheres and are therefore not directly comparable with our values. The fact that the difference between the two curves is sensibly uniform is to be expected. The absence in Gibson's plot of clear evidence of breaks at the two critical concentrations is at first sight disturbing. This failure to conform to our results, however, is probably due to two facts: first, Gibson's compressibility measurements are slightly less precise than ours, and second, the distribution of the plotted points would tend to obscure rather than enhance the appearance of the breaks in question. In concluding the description of this graph attention may be called to the fact that Scott and Blair (9) also found definite breaks in the variation of the magnetic susceptibility of lithium chloride solutions with concentration at concentrations $n_w = 10$ and 6.

The anomalies of lithium bromide solutions are more striking than those of the chloride solutions. In the ϕ–c plot of these bromide solutions there appear to be three critical concentrations as follows:

Intersection of curves	*Values of n_w*
α–β	18
β–γ	8
γ–δ	5

The first of these concentrations cannot be determined with the same certainty as the others, but the value 18 is unquestionably a minimum figure.

Evidence bearing on the irregularities in these concentrated bromide solutions has been reported by other investigators. Hüttig and Keller (4) in 1925 published the results of an extensive series of density measurements on the basis of which they concluded that the relation of ϕ to n_w undergoes abrupt changes when $n_w = 6$, 30, and 75. Discontinuities were believed to exist at practically the same concentrations in similar plots of the molar refractivity and absorption coefficients against log n_w. Prompted by the critical discussion of these conclusions, Hüttig and Kükenthal (5), three years later, reported the results of new density and composition measurements at 20°C. which were not entirely in agreement with the earlier series. From the new data it was concluded that the only unambiguous discontinuity in the ϕ–log n_w plot occurs when $n_w = 6$. The ϕ and c values (at atmospheric pressure) calculated from the published data of these investigators are included also in figure 1, where they appear as the middle curve. In order to simplify the mechanical features of the graph it was necessary, in plotting the comparison data, to increase all the ϕ values by exactly

0.500 cc. There is an unmistakable resemblance between the two ϕ–c plots, a fact which we have attempted to bring out more clearly by drawing through the plotted points depicting the data of Hüttig and Kükenthal curves similar to those representing our own measurements. It appears that the ϕ–c plot representing the data of these investigators agrees in general with the plot of our data, but does not necessarily confirm our conclusion regarding the exact location of the three discontinuities.

Although no complete interpretation of these unusual irregularities in the concentrated solutions of lithium chloride and bromide is possible at this time, a number of general conclusions may be suggested. The traditional approach to a problem of this kind would be to assume that the irregularities in question arise from alterations in the degree of hydration of the lithium ion which is common to both salts. Thus, Hüttig and Keller, in order to account for the supposed irregularities in their solutions at concentrations $n_w = 6, 30$, and 75, argued that these critical concentrations corresponded to the theoretical composition of one ($n_w = 6$), two ($n_w = 30$), and three ($n_w = 76$) layers of water molecules packed around the lithium ion. From the standpoint of our results, this simple hydration hypothesis falls down, because the critical concentrations of the solutions of the chloride and bromide are not the same.

We would hardly expect an hydration hypothesis to be applicable to solutions of high concentration where a large fraction of the ions must be in contact with each other. It seems much more to the point to consider the question whether irregularities in these solutions can be ascribed simply to changes in the arrangement or packing of the ions (i.e., the domain of the solute). In attempting to formulate a tentative answer to this question we shall make use of an argument which was developed in paper I. It may be recalled that the quantities ϕ and $(\bar{B} + f)$ have only an *apparent* physical significance, and that a change in magnitude of either of these quantities is possibly the net result of variations in two factors, one related to the domain of the solute and the other related to the number of solvent molecules which, under the influence of ionic forces, have suffered a contraction in volume. In the case of ϕ the possible magnitude of changes in either factor may be of the same order, and therefore it would be impossible from the nature of the changes in ϕ to determine which factor is responsible for the change. On the other hand, in the case of $(\bar{B} + f)$ the possible variation in the compressibility of the solute is so small relative to the possible change in the second factor that the individual effects of the two factors can be partially distinguished. In brief, unless the variation in $(\bar{B} + f)$ with concentration is extremely small, it can be assumed to involve a change in the number of molecules of water in the contracted state.

If we examine the $(\bar{B} + f)$–c plots with this method of analysis in mind, we find no evidence of unusual variation in the amount of water in the contracted state. This negative conclusion is important, because it rules out of consideration one explanation of the irregularities in the ϕ–c plots and therefore means that changes in the domain of the solute must occur in the concentrated solutions. As a matter of fact a more detailed application of this argument leads to the conclusion that the actual changes in the domain of the solute are much greater than the variation in ϕ.

No inferences can be drawn regarding the changes in packing of the ions and water molecules, which we assume to be the cause of the change in the domain of the solute. It is worth noting, however, that Bassett and his collaborators (1), in seeking to elucidate the structures of various lithium salt hydrates and complexes, have been obliged to postulate the existence of various types of polynuclear cations and even complex anions containing lithium. If such complexes exist in the solid state, they doubtless exist also in solution, and it may be suggested that a certain complex may be stable in solution only in a limited concentration range and that the characteristic properties of the several concentration regions depend on the complex or complexes present. The magnetic susceptibility measurements of lithium chloride mentioned above can be looked upon as supporting this viewpoint. The susceptibility of the salt was found to be constant in dilute solutions up to the concentration $n_w = 10$, and to be constant also in very concentrated solutions, $n_w < 6$. In other words, one structural arrangement or complex may be supposed to be stable in dilute solution, another in very concentrated solutions, and in the concentration range (β) a transition between these two types of arrangement may be supposed to take place. It is likely that a determination of the susceptibilities of the bromide solutions would throw some light on these more complex solutions and possibly on the problem as a whole.

SUMMARY

New measurements of the densities and compressibility coefficients of concentrated solutions of lithium chloride and bromide are reported. On the basis of these and previous measurements, the irregular properties of the concentrated solutions of these electrolytes are discussed.

A graphical method for calculating the factor

$$f\left[=\left(\frac{\partial\phi}{\partial c}\right)_P \frac{dc}{dP}\right]$$

is described.

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COMMUNICATION TO THE EDITOR

ON THE $(C—C)_{diam}$ BOND ENERGY

In a recent communication (Lasareff, W.: J. Phys. Chem. **39**, 913 (1935)) with the above title, there was suggested a value of 123 Cal. for the energy of the C—C bond. Since this value is so much larger than that currently accepted, and since this quantity is of great importance in thermochemistry, it seems worth while to examine some of the assumptions made in its derivation. It was assumed that the most probable value for the heat of sublimation of carbon is 154 ± 10 Cal. The recent work of W. Lozier(Phys. Rev. **46**, 268 (1934))on the heat of dissociation of CO leads to two alternate values for this heat of sublimation, 136 ± 2 and 182 ± 2 Cal. Thus the magnitude of this quantity is still rather uncertain. Even if 154 Cal. is accepted, it does not necessarily follow that the energy of the C—C bond is 123 Cal. In the thermodynamic cycle that was used, it was assumed that the diamond dissociates to give ^5S atoms, which then drop to the ^3P state. There is, however, another possibility, that the quadrivalent carbon in diamond, presumably in the ^5S state, may dissociate adiabatically into ^3P atoms. This has been more completely discussed in previous work (Kistiakowsky, G. B , and Gershinowitz, H.: J. Chem. Physics, **1**, 432 (1933); Gershinowitz, H.: Thesis, Harvard University, 1934). If this should be the actual process, the energy of the C—C bond would be 77 ± 5 Cal., which is in much better agreement with the available data than is the larger figure. Even though the energy of a bond is not a constant which is entirely independent of the compound in which the bond occurs, an energy of 123 Cal. for the C—C bond in diamond seems to be quite incompatible with the energy of dissociation of cyanogen into cyanide radicals (77 ± 4 Cal.) (see preceding reference), and with the energy of activation for the decomposition of ethane into methyl radicals (79.5 Cal.) (Rice, F. O., and Johnston: J. Am. Chem. Soc. **56**, 214 (1934)). Neither the theory nor the data from which the value of 123 Cal. has been derived is sufficiently certain to allow one to prefer it to other values.

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FLOTATION OF GALENA AND CHALCOCITE OF NEAR-COLLOIDAL SIZE WITH POTASSIUM AMYL XANTHATE AND AMYL DIXANTHOGEN

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In the beneficiation of ores by ore-dressing processes the treatment of the finest portion of an ore has always been a problem difficult, if not sometimes impossible, of solution. Flotation has proved no exception to this rule. In the "near-colloidal" size-range of mineral particles embracing the entire scale from 5 microns to the size of the truly colloidal particles recovery by flotation has been found to be very unsatisfactory (1, 5).

A study directed to improve the flotation behavior of these particles has been carried on at the Montana School of Mines since 1931. It resulted in the discovery of a successful experimental solution of the problem of flotation of near-colloidal pulps (6). By adding the collector into the pebble mill, so that it is present while the minerals are being ground, satisfactory flotation results can be obtained. This holds true for a number of collectors that comprise a group of the most common ones and of some of their less common derivatives (6).

The present paper deals with the investigation of the effect of some arbitrary variables on the flotation behavior of two mineral mixtures (galena–aplite and chalcocite–aplite) when the collector is present during the grinding.

The variables investigated are: (a) the effect of increasing amount of collector; (b) the effect of some alkaline pH-modifying agents; and (c) the effect of substituting a "neutral" grinding atmosphere for air atmosphere. The study of the effect of the three variables was confined to two collectors: potassium *n*-amyl xanthate and its oxidation derivative, *n*-amyl dixanthogen (*n*-amyl thioformate disulfide).

EXPERIMENTAL METHOD

The grinding and flotation procedure employed was such that all conditions were kept as nearly constant as was experimentally possible. Accordingly the minerals used, galena, chalcocite, and aplite (consisting chiefly of quartz and orthoclase, with a little plagioclase), were specially purified and sized to 20/100 mesh. In all the tests 70 g. of the sulfide mineral and 280 g. of the gangue (aplite) were charged together with the collector into an assay-size Abbé porcelain pebble mill with 225 cc. of water and ground for twenty-one hours. This grinding reduced all the minerals to the size of 3 microns or finer. Flotation of the ground mixtures was conducted in a 500-g. Fahrenwald flotation machine. When necessary, terpineol[1] was used as a frother in amount sufficient (0.05 to 0.20 lb. per ton) to produce froth requisite for normal rate of flotation. Flotation products were analyzed for the metal of the sulfide mineral.

In the tests in which the minerals were ground in a "neutral" atmosphere, i.e., in virtual absence of oxygen, the mill atmosphere was successively evacuated and refilled with nitrogen, grinding being done in an evacuated mill after two flushings with nitrogen. Disregarding the oxygen adsorbed on solid surfaces and that dissolved by water, the oxygen remaining in the mill atmosphere was calculated to be approximately 0.000045 mole. Flotation in these tests was conducted in air, as usual.

Effectiveness of flotation was quantitatively evaluated by means of the selectivity index (3). Recovery of the sulfide mineral was calculated for each test. For graphic presentation of the experimental results the selectivity index was plotted as ordinate against the arbitrary variable as abscissa.

The experimental method outlined above has been found useful in fields of research outside that for which it was originally designed. Thus, by means of this method it was possible to undertake an investigation from which a hypothesis for the non-flotation of minerals of near-colloidal size was formulated (7). Also, it was found possible to substantiate some conclusions regarding the formation of reaction products of the reagent with the mineral base on a more direct study of their formation (4).

EXPERIMENTAL RESULTS

Effect of increasing amount of collector

A series of tests was conducted in which progressively greater amounts of the collectors were used while all other conditions were kept constant. The results for galena and chalcocite with potassium amyl xanthate and with amyl dixanthogen at a "natural" pH (i.e., that obtaining in the pulp after the completion of the flotation operation when no pH modifiers are used) are presented in tables 1 and 2, and graphically in figure 1. In figure 1 along the abscissa the quantity of potassium xanthate (pounds per ton) is plotted. In order to make the results obtained with dixanthogen strictly comparable to those obtained with potassium xanthate, the amounts of dixanthogen used are plotted in terms of potassium xanthate containing xanthate radical $(-\mathrm{S}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\mathrm{OC_5H_{11}})$ equivalent to that contained in dixanthogen.

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[1] Terpineol does not appear to affect the effectiveness of flotation but merely its rate.

A very curious phenomenon was encountered in the case of the test in which dixanthogen equivalent to 32.0 lb. of potassium xanthate per ton was used for flotation of galena. After grinding, the pulp appeared pinkish white (color of ground aplite), indicating absence of galena within it (usually the presence of galena is indicated by the gray color of the pulp). The galena was finally discovered among the washed pebbles in the form of a hard, compressed, nearly perfect sphere. In addition, there were occasional fragments of compressed galena of irregular shapes adhering to the rubber gasket of the cover of the pebble mill. Upon charging of the white pulp into the flotation machine, instead of the usual froth a greasy and

TABLE 1

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of galena-aplite mixtures

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.4		24.6	14.4	1.4	17.9
1.4		31.0	14.2	1.8	17.5
2.0		39.0	5.9	3.3	71.7
2.8		50.2	0.39	17.5	98.10
2.8		51.3	0.35	19.0	98.41
2.8		44.7	0.21	21	99.08
4.0		45.9	0.20	22	99.12
4.0		45.4	0.18	23	99.21
5.7		46.2	0.30	18.3	98.68
5.7		44.4	0.26	18.7	98.89
8.0		45.0	0.30	17.7	98.61
8.0		46.2	0.30	18.2	98.56
11.4		47.2	0.17	25	99.21
16.0		56.0	0.22	27	99.00
32.0		56.6	0.16	33	99.23
	1.4	18.0	15.0	1.1	4.1
	2.8	48.0	0.40	17.3	98.14
	4.0	56.0	0.40	20	98.11
	5.7	45.4	0.48	14.1	97.76
	8.0	44.8	0.36	16.1	98.23
	16.0	51.8	0.36	19.1	98.32
	32.0	79.3	0.11	98	99.38

TABLE 2

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite–aplite mixtures

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.4		24.0	12.5	1.5	9.6
1.0		30.4	13.2	1.8	16.8
2.0		41.2	2.17	6.4	89.8
4.0		36.2	1.13	7.8	94.6
4.0		44.3	1.13	9.6	93.8
8.0		38.1	3.46	4.6	81.8
8.0		31.3	3.20	4.0	84.0
16.0		34.9	1.73	6.0	90.2
16.0		41.3	2.98	5.4	82.7
	0.55	20.7	13.1	1.3	5.9
	1.4	40.5	5.1	4.0	72.0
	2.8	47.9	1.25	10.1	93.3
	5.5	39.8	1.28	8.0	92.7
	11.0	38.1	3.14	4.8	82.6
	22.0	41.6	3.7	4.9	79.8

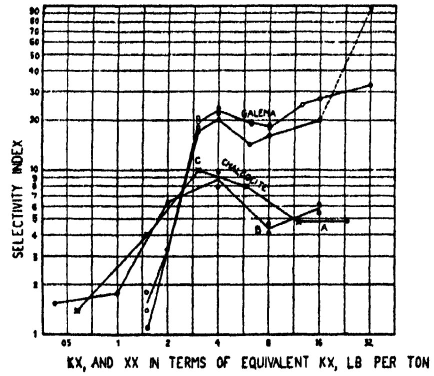

FIG. 1. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF GALENA–APLITE AND OF CHALCOCITE–APLITE MIXTURES

✖ chalcocite with amyl dixanthogen (XX); ⊕ chalcocite with potassium amyl xanthate (KX); ● galena with amyl dixanthogen (XX); ○ galena with potassium amyl xanthate (KX).

shiny film formed, which was scraped off. The pulp remaining in the machine after this operation was termed tailing, and analyzed for lead. In table 1 the data for the concentrate for this test were calculated by difference from the amount of galena originally put in. The selectivity index obtained for this test is not entirely comparable to the other tests of the series because concentration was not effected in the flotation machine but in the pebble mill during grinding. The selectivity index is so high, chiefly because the concentrate contained very little gangue.

In the case of both galena and chalcocite the results obtained with potassium xanthate and with dixanthogen agree within the limits of experimental error, so that only one curve for both the reagents could be drawn. If this is warranted and the action of both the reagents on the mineral can be assumed identical, one could postulate that the flotation-inducing non-polar coatings produced on the mineral by the reaction of the reagents with the mineral are the same for dixanthogen and potassium xanthate. This speculation is confirmed by the more direct study of the reaction of dixanthogen and of potassium xanthate with chalcocite and with galena (4).

The peculiar shape of the curves for chalcocite in figure 1, that is, the dip of the curves with amounts greater than 4.0 lb. per ton, and the rise with amounts greater than 8.0 lb. per ton, may be explained on the basis of the reaction products formed. Froths from tests in which the amounts of reagents were used that corresponded to the maxima and the dips of the curves yielded upon extraction with benzene different reaction products. These products were identified with those obtained by F. Dewey (6, 5): at point *A* of the curve as cuprous xanthate (Cu_2X_2), and at point *C* as a compound of the type $xCu_2S \cdot yCu_2X_2$. From the knowledge of the reaction of xanthate and dixanthogen with chalcocite given elsewhere (4), the following explanation is proposed:[2] At point *A* the reaction product on the mineral surface is copper xanthate. As the amount of the reagent is decreased while the extent of chalcocite surface remains constant, deficiency of xanthate radical for the formation of Cu_2X_2 causes the formation of complex compounds containing less xanthate per molecule (of the type $xCu_2S \cdot yCu_2X_2$). These compounds are more non-polar; hence they induce better flotation and the curve rises to *C*. With less than the amount of reagent at *C* there is insufficient reagent to coat effectively the mineral surface exposed and flotation is incomplete, as is evidenced by the drop in the curve.

The non-conformance of the dixanthogen and the xanthate curves in the region of high amounts of reagent might not be entirely due to experimental error. When high amounts of potassium xanthate are used the hydroxyl-ion concentration (OH^- ion is derived from hydrolysis of xanthate and from the reaction of xanthate with the oxidation coating of chalcocite, which is a basic carbonate) is possibly increased enough to cause the formation of copper monothiocarbonate (4), which is presumably more polar than the copper xanthate; hence the depression of the xanthate curve at point *B* below the dixanthogen curve.

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[2] After Franklin Dewey (2).

It may be conjectured that the dip and rise in the galena curves are also due to the formation of different reaction products. Positive evidence for this is not available to date.

It is noteworthy that the rise and dip in the galena and in the chalcocite curves occur at approximately the same amounts of reagents.

Effect of alkaline pH modifiers on flotation of galena

Using galena–aplite mixtures, a series of tests was conducted in which some pH modifiers were added with the collector into the pebble mill. Flotation was carried on as usual. Table 3 summarizes the results of these tests. Unfortunately in most cases it was impossible to determine pH for the different amounts of modifiers used; the pulp was highly dispersed so that clear solution could not be obtained for colorimetric determinations of pH by any method of filtration or clarification available in the laboratory.

It is clear from an examination of the results in table 3 that hydroxyl-ion concentration in the grinding system is very injurious to subsequent flotation. The action of all of the pH modifiers seems to affect flotation adversely if enough modifier be used. Because with a larger amount of collector more modifier is needed to inhibit flotation of galena, it may be conjectured that the action of the modifier is to consume or change the collector or reaction products of the collector with galena so as to render them useless for flotation.

That flotation of galena with amyl dixanthogen is also adversely affected by high pH is shown by the tests given in table 4.

Effect of pH modifiers on flotation of chalcocite

A series of tests was conducted in which chalcocite–aplite mixtures were floated using increasing amounts of potassium xanthate and of dixanthogen with 20.0 lb. of lime per ton. The results are presented in table 5 and in figure 2.

Whereas the use of pH modifiers was injurious to flotation of galena, in the case of chalcocite, lime, one such modifier, seems to be highly beneficial. Again, as in the case when no modifiers were used, within limits of experimental error the results obtained with both the potassium xanthate and with dixanthogen appear to indicate that the action of the two reagents is identical. Conformance of the two curves in the region of large amount of reagents is better than in figure 1 for chalcocite. This is possibly because the concentration of hydroxyl ion remains substantially the same for both reagents, as an excess of hydroxyl ion is present, derived from the lime added.

TABLE 3

Effect of some pH modifiers on flotation of galena–aplite mixtures with potassium amyl xanthate

POTASSIUM AMYL XANTHATE	POTASSIUM HYDROXIDE	CALCIUM* HYDROXIDE	SODIUM CARBONATE	CONCENTRATION OF TOTAL AVAILABLE OH	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
					Concentrate	Tailing		
lb. per ton	*lb. per ton*	*lb. per ton*	*lb. per ton*	*equiv. per liter*				*per cent*
4.0					45.4	0.18	23	99.21
4.0	5.2‡			0.0058	16.6	14.9	1.1	18.6
4.0	10.5§			0.0115	16.2	14.5	1.1	18.1
4.0	26.2¶			0.0288	14.8	14.9	1.0	20.3
4.0		4.0		0.0058	27.6	4.8	2.8	81.0
4.0		4.0		0.0058	36.2	7.7	2.7	62.9
4.0		8.0		0.0115	14.4	14.2	1.0	16.6
4.0		20.0		0.0288	25.2	12.5	1.6	39.0
4.0		40.0		0.0576	27.0	7.0	2.3	71.3
4.0			4.0	0.0053†	43.2	0.68	11.2	96.37
4.0			8.0	0.0106	18.0	14.5	1.1	17.5
4.0			20.0	0.0265	17.4	14.4	1.1	13.2
4.0			40.0	0.0530	17.4	14.9	1.1	13.9
8.0					46.2	0.30	18.2	98.56
8.0		4.0		0.0058	48.2	0.34	17.8	98.37
8.0		8.0		0.0115	45.2	0.22	21	98.96
8.0		20.0		0.0288	48.4	0.28	19.8	98.67
8.0		40.0		0.0576	45.0	0.48	14.0	97.82
16.0					56.9	0.22	27	99.00
16.0		8.0		0.0115	47.2	0.18	24	99.20
16.0		20.0		0.0288	48.0	0.28	19.5	98.67

* Commercial slaked lime, 76 per cent pure.

† Assuming complete hydrolysis of sodium carbonate.

‡ Equivalent to 4.0 lb. $Ca(OH)_2$ per ton.

§ Equivalent to 8.0 lb. $Ca(OH)_2$ per ton.

¶ Equivalent to 20.0 lb. $Ca(OH)_2$ per ton.

TABLE 4

Effect of high pH on flotation of galena with amyl dixanthogen

	DIXANTHOGEN EQUIVALENT TO 4.0 LB. POTASSIUM XANTHATE PER TON	
	20.0 lb. calcium hydroxide per ton	No pH modifier
Per cent lead in concentrate	37.0	56.0
Per cent lead in tailing	5.8	0.40
Selectivity index	3.2	20
Recovery, per cent	75.2	98.11

TABLE 5

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite-aplite mixtures with 20.0 lb. of lime per ton

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.0		11.7	13 6	0.9	7.9
1 6		24.2	13.3	1.5	5.6
2.0		52.4	0 66	16.4	95.6
2 6		55.4	0.43	22	97.5
2.6		55.7	0 50	20	97.5
4.0		47 0	0.31	19.9	97.2
4 0		41.8	0.33	16 8	98.3
8.0		43 6	0.31	18.3	98 5
9.7		43.2	0 29	18 6	98.5
32.0		49.0	0.16	27	98 8
	1.6	15.3	13.40	1.1	5 3
	2.6	56 6	0.47	22	97 6
	5.5	46.0	0.47	15.6	97 8
	5.5	46.6	0.52	15.2	97 8
	7 2	47.0	0.36	18.4	98.2
	11 0	44 7	0.31	18.3	98.5

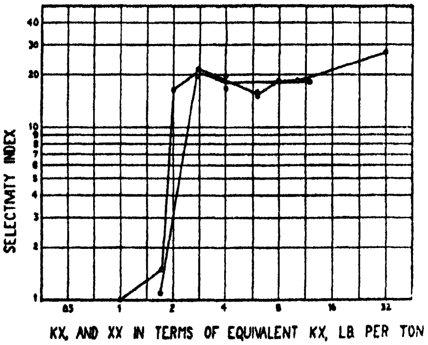

FIG. 2. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF CHALCOCITE-APLITE MIXTURES WITH 20.0 LB. OF LIME PER TON (COMPARE WITH FIGURE 1)

● Chalcocite with amyl dixanthogen (XX) and 20.0 lb. CaO per ton; ○ chalcocite with potassium amyl xanthate (KX) and 20.0 lb. CaO per ton.

In order to investigate fully the effect of lime on flotation of chalcocite a series of tests was conducted in which both the amount of potassium xanthate and the amount of lime were the arbitrary variables. These tests are presented in table 6. The results are presented graphically in figure 3, in which the selectivity index is plotted as the coördinate perpendicular to the plane of the paper, and contour lines are drawn connecting projections in the plane of the paper of points of equal selectivity index.

The effect of potassium hydroxide and of lime on flotation of chalcocite with constant amount of amyl dixanthogen is shown by table 7 and by figure 4. Excessively high amounts of potassium hydroxide were necessary to induce the requisite pH. This is possibly because the hydroxide was consumed by reaction with the gangue.

TABLE 6

Effect of varying amounts of potassium amyl xanthate and of lime on flotation of chalcocite-aplite mixtures

POTASSIUM AMYL XANTHATE	CALCIUM OXIDE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.8	4.3	47.6	0.85	12.2	95.5
2.0	8.0	48.6	0.70	13.8	96.3
4.0	8.0	51.6	1.76	9.5	91.0
8.0	8.0	51.7	1.09	12.1	94.7
16.0	8.0	49.5	0.52	16.5	97.4
1.4	10.3	25.9	13.4	4.9	11.5
2.0	12.0	56.2	0.43	22	96.8
4.0	12.0	51.6	0.45	18.8	97.7
16.0	12.0	46.3	0.34	18.6	97.1
1.3	13.1	16.3	14.0	1.1	1.7
32.0	14.3	47.8	0.24	23	99.5
7.2	15.4	51.9	0.38	21	98.2
1.7	16.0	32.4	12.4	6.2	16.8
2.3	16.0	48.5	0.49	18.9	98.0
16.0	17.1	48.6	0.32	20	98.4
5.7	18.3	47.0	0.34	19.0	98.6
2.9	18.9	48.5	0.39	18.5	98.0
5.7	22.9	39.8	0.44	13.7	97.8
5.7	28.6	45.2	0.19	24	99.1
11.4	28.6	51.6	0.29	24	98.6

Effect of "neutral" grinding atmosphere

A series of tests was conducted in which the minerals were ground in a pebble mill whose atmosphere was practically devoid of oxygen. Oxygen was removed by the procedure given earlier in the paper. In the series of tests using chalcocite, 20.0 lb. of lime per ton was added together with the collector, whereas in galena tests no modifying agents were used. The results are presented in tables 8 and 9 and in figure 5.

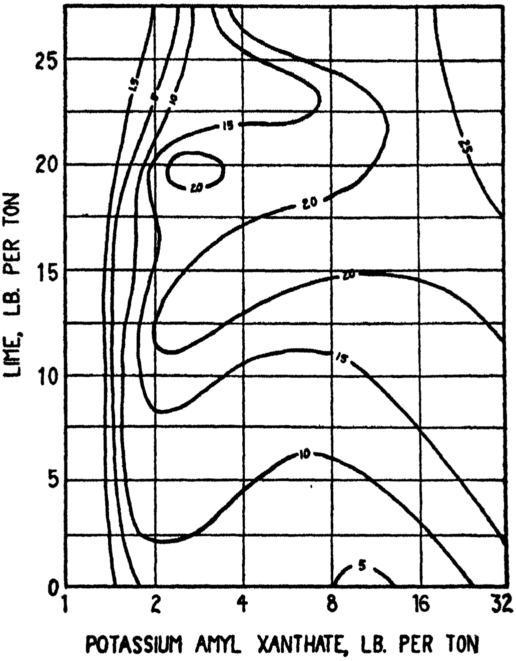

FIG. 3. EFFECT OF VARYING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF LIME ON FLOTATION OF CHALCOCITE-APLITE MIXTURES

TABLE 7

Effect of pH resulting from increasing amounts of potassium hydroxide and of lime on flotation of chalcocite-aplite mixtures with amyl dixanthogen equivalent to 5.4 lb. of potassium amyl xanthate per ton

POTASSIUM HYDROXIDE	CALCIUM OXIDE	pH	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
			Concentrate	Tailing		
lb. per ton	*lb. per ton*					*per cent*
23.0*		10.2	39.6	0.62	11.2	96.9
57.0		11.7	39.8	0.46	13.1	97.6
114.0		12.4	38.9	0.59	11.3	96.8
	4.0	8 6	40.2	0.67	11.2	96.4
	11.4	10.2	39.1	0.27	17.1	98.7
	20.0	11.2	46.0	0.47	15.6	97.8
	40.0	12.0	41.9	0.36	16.0	98.3

* Amount yielding OH^- ions equivalent to OH^- ions yielded by half as many pounds of CaO per ton.

Again, as in figures 1 and 2 and in tables 1, 2, and 5 the two reagents, dixanthogen and potassium xanthate, seem to yield results for which only one curve need be drawn for a given mineral. Also, the shapes of the

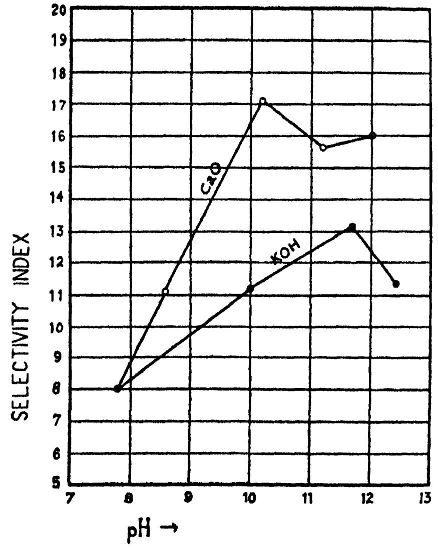

FIG. 4. EFFECT OF pH RESULTING FROM INCREASING AMOUNTS OF POTASSIUM HYDROXIDE AND OF LIME ON FLOTATION OF CHALCOCITE-APLITE MIXTURES WITH AMYL DIXANTHOGEN EQUIVALENT TO 5.4 LB. POTASSIUM AMYL XANTHATE PER TON

TABLE 8

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite-aplite mixtures ground in absence of air

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.46		No flotation		1 0	0
0.73		36 6	1 06	.8.1	95.1
1.14		45.9	0 61	13.8	98 4
1.6		53 6	0.19	27	99 0
2.9		46 6	0.15	29	99.3
2.9		48 1	0.14	30	99.4
2.9		48.3	0.12	32	99.5
5 5		48.3	0.13	32	99.3
11.4		50.1	0.069	46	99.7
	0.46	No flotation		1.0	0
	0.9	43.5	0.29	18.7	98.6
	1.6	44.9	0.18	25	99.1
	2.9	48.5	0.122	33	99.5
	5.5	49.8	0.11	26	99.4
	11.4	48.9	0.077	42	99.6

TABLE 9

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of galena–aplite mixtures ground in absence of air

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.57		No flotation		1.0	0
1.0		No flotation		1 0	0
2 0		58 9	0.30	25	98.54
4.0		53.6	0 21	26	99.06
8.0		55 8	0.18	30	99.20
16.0		54.9	0.18	29	99.17
32.0		58.1	0.19	33	99.24
	1 0	42.4	3.6	4.7	85 3
	1.4	54 6	0.80	13 3	96.31
	2.8	52 0	0.30	21	98.65
	5 7	54 6	0.165	30	99 27
	8 0	54 2	0.124	35	99 45
	32 0	63.9	0 103	49	99 47

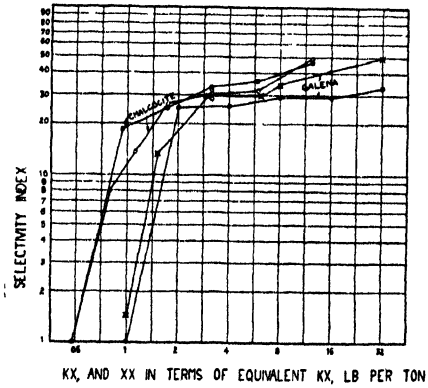

FIG. 5. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF CHALCOCITE–APLITE AND OF GALENA–APLITE MIXTURES GROUND IN ABSENCE OF AIR (COMPARE WITH FIGURES 1 AND 2)

● chalcocite with amyl dixanthogen (XX) and 20 lb. CaO per ton; ○ chalcocite with potassium amyl xanthate (KX) and 20 lb. CaO per ton; ✖ galena with amyl dixanthogen (XX); ⊕ galena with potassium amyl xanthate (KX).

curves for galena and for chalcocite are similar, as they were in figure 1. However there is no dip in the curves as there was in those of figure 1.

If one compares the chalcocite curves of figure 2 with those of figure 5, it can be noted that to induce flotation when chalcocite is ground in the absence of air the amount of reagent necessary is approximately half that required to induce flotation when it is ground in presence of air.

Apparently no such simple relation exists in the case of galena, although markedly less reagent is required to induce flotation when galena is ground in "neutral" atmosphere than that required when it is ground in air.

It is to be noted that, likewise, to induce flotation of chalcocite the amount of reagent required is approximately one half that necessary in the case of galena.

All these facts may have a significance in the interpretation of floatability in the light of reaction products. But such an interpretation cannot be given at present, because our knowledge of the reactions has not as yet been put on a strictly quantitative basis.

The results obtained when the minerals are ground in neutral atmosphere are superior to any hitherto obtained in this research. This seems to indicate that oxygen has some undetermined injurious action when it is present, as it always is in practice, in the grinding atmosphere.

CONCLUSIONS

1. The action of potassium amyl xanthate and of amyl dixanthogen on galena and on chalcocite of near-colloidal size appears to be identical when the mineral is ground in air.
2. Concentration of hydroxyl ion influences profoundly the flotation of sulfides, and its influence is specific to each of the sulfides.
3. High pH is conducive to better flotation of chalcocite of near-colloidal size with amyl dixanthogen and with potassium amyl xanthate, whereas it is destructive to flotation of galena with the same reagents.
4. It is proposed that the hydroxyl radical influences the formation of reaction products whose formation in turn affects flotation of the sulfide mineral.
5. Under the experimental conditions employed, oxygen in grinding has a noticeable injurious effect on the flotation of chalcocite and of galena with potassium amyl xanthate and with amyl dixanthogen, as evidenced by the results obtained when the minerals are ground in virtual absence of oxygen; they are superior to any hitherto obtained in this research.
6. The action of potassium amyl xanthate and of amyl dixanthogen on galena and on chalcocite appears to be identical when the mineral is ground in a "neutral" atmosphere, i.e., in virtual absence of air.

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THE KINETICS OF THE REACTION BETWEEN PERMANGANATE AND MANGANOUS IONS[1]

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INTRODUCTION

The reaction between permanganate and manganous ions (the Guyard reaction (1); manganese dioxide is formed) is slow in acid solutions, even at high temperatures. This is a familiar fact, since the recognition of the end point in the permanganate–oxalate titration depends on it. The present paper contains a brief description of the writer's recent observations showing that the reaction has an incubation period and that it is autocatalytic. For the sake of continuity, the main observations and general conclusions will be given first, followed by the experimental details. In order to facilitate cross reference, corresponding sections and the figures illustrating them will be given the same numbers (sections A–I to A–VIII, sections B–I to B–VII, and figures 1 to 7). In the present discussion a solution containing manganous and permanganate ions will be referred to as a Guyard solution. The heterogeneous mixture resulting from such a solution will be called a Guyard mixture.

A–I. This investigation is a side product of an unpublished study of the permanganate–thiosulfate reaction, undertaken by the writer. It is known that each mole of thiosulfate ion reduces one equivalent of a mild oxidizing agent, such as iodine. It reduces a larger number of equivalents when reacting with manganese dioxide. Finally, thiosulfate ion reduces a still larger number of equivalents when it reacts with permanganate ion.

It was to be expected, therefore, that, if a small amount of thiosulfate ion is added to an acid Guyard mixture, the quantitative results should depend on the age of the latter at the time of mixing, in other words, on the amount of manganese dioxide formed at the expense of the permanganate. This prediction was tested and verified in a series of experiments. The curve obtained in this series of experiments gave the first indication that the reaction between permanganate and manganous ions is autocatalytic in acid solution. This was supported by visual observations on the Guyard solution; the latter remained clear and purple for a measurable time (incubation period), after which the reaction proceeded at a rapidly increasing rate.

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[1] This investigation is a part of a project carried out on a grant from the National Research Council, to which the writer takes pleasure in expressing his obligation.

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A–II. In order to study the effect of acid on the Guyard reaction, visual observations were made on mixtures containing the same amounts of potassium permanganate and manganous sulfate, but varying amounts of perchloric or sulfuric acid. It was found that both the incubation period and the total reaction time were proportional to the concentration of the perchloric acid. When sulfuric acid was used, the results were complicated by the tendency of sulfate ion to shunt the reduction of permanganate by manganous ion into another reaction path. This tendency was linked with the formation of manganic sulfate complex ion.

A–III. Visual observations were next carried out on mixtures containing constant amounts of potassium permanganate, manganous sulfate, and sulfuric acid, and varying amounts of potassium fluoride. It was found that fluoride ion also modifies the process of reduction of permanganate ion. The effect of fluoride ion was stronger than that of sulfate ion, and this was linked with the greater tendency to form the manganic fluoride complex.

A–IV. The observations described in sections A–II and A–III were visual and therefore subjective, to a certain extent. After several attempts to develop an objective method of following the Guyard reaction, the writer decided to use oxalic acid for this purpose. (The use of thiosulfate ion was avoided because the stoichiometry of the several reactions is not sufficiently well understood.) The oxalic acid method depends on the fact that under certain conditions the acid is oxidized by manganese dioxide but not by permanganate ion. In the presence of a small excess of manganous ion both react rapidly with the acid, forming manganic oxalate complex. In this fast reaction one half of the manganese dioxide is reduced by the acid, whereas very little of the permanganate ion is reduced by the oxalic acid; it is practically entirely reduced by the manganous ion:

$$MnO_4^- + 4Mn^{++} + 10H_2C_2O_4 = 5Mn(C_2O_4)_2^- + 4H_2O + 12H^+ \quad (1)$$

$$2MnO_2 + 5H_2C_2O_4 = 2Mn(C_2O_4)_2^- + 2CO_2 + 4H_2O + 2H^+ \quad (2)$$

It follows that, if excess oxalic acid is added to a Guyard mixture, the loss of oxidizing titer will give a measure of the amount of manganese dioxide formed at the expense of the permanganate ion. It will be shown in the experimental part of this paper that the oxalic acid method is applicable only when the concentration of the manganous ion is low. If the concentration of manganous ion is high, the manganese dioxide will dissolve in oxalic acid without reduction.

A–V. With the use of oxalic acid it was shown once more that the Guyard reaction in acid solution is autocatalytic. It was also shown that the rate of reaction in a Guyard mixture was increased by a decrease in acidity or by an increase in the concentration of either the manganous or the permanganate ion.

A–VI. In an attempt to find the cause of the autocatalysis, the assumption was tested that the manganese dioxide formed in the reaction was the responsible agent. In several series of experiments manganese dioxide was added to the initial solution. It was found that this procedure eliminated the incubation period and accelerated the reaction. It was further found that the effectiveness of the manganese dioxide as a catalyst depended on the mode of its preparation; the solid prepared in neutral solution was much more effective than that prepared in acid solution. From visual observations it was clear that the "neutral" solid was much more highly dispersed than the "acid" solid.

A–VII. It was realized that the difference between the catalytic activities of manganese dioxide prepared in neutral and in acid solution might have been due in part to a difference in chemical composition. The two solids were analyzed iodometrically and were both found to contain tetravalent manganese only. If there was any difference at all in the composition of the "neutral" and "acid" manganese dioxide, it could have been only in the degree of hydration of the oxide.

EXPERIMENTAL

B–I. The reaction of thiosulfate ion with excess acid mixture of permanganate and manganous ions. In this series of experiments the following procedure was used: 150 cc. of a solution was prepared containing 0.00333 *M* potassium permanganate, 0.00867 *M* manganous sulfate, and 0.0666 *M* sulfuric acid. At the time t after mixing, 10 cc. of 0.01 *M* sodium thiosulfate was added. The thiosulfate was oxidized rapidly in all cases. Thirty seconds later aqueous potassium iodide was added (the time of addition of potassium iodide is immaterial). The iodine formed was titrated with standardized sodium thiosulfate solutions. The ratio

$$\frac{\text{number of equivalents of oxidizing agent reduced}}{\text{number of moles of thiosulfate added}}$$

was calculated from the observed loss of oxidizing titer.

The experimental results are shown in figure 1. Briefly, they can be summarized as follows: Freshly prepared solutions, containing only permanganate and manganous ions, lose four equivalents of oxidizing agent per mole of thiosulfate added. Old solutions, containing only manganese dioxide and manganous ion, lose only two equivalents of oxidizing agent. Intermediate results are obtained with intermediate solutions. The shape of the curve gives a clear indication of the autocatalytic nature of the Guyard reaction. This is verified by the visual observations given in figure 1. In this particular Guyard solution the color remained unchanged about twenty seconds.

If the manganous sulfate is omitted (experiment 2062, figure 1), thiosulfate ion reduces six equivalents of oxidizing agent. The deviation of experiment 2062 from the main series is significant: although the manganous ion reacts slowly with permanganate ion, it exerts a strongly modifying influence on the rapid permanganate–thiosulfate reaction.

B–II. Visual observations on the effects of acid and of sulfate ion on the rate of the Guyard reaction. The effect of perchloric acid is shown in figure 2 (lines 2090). In each experiment of this series the initial solutions contained the same amount of permanganate and manganous ions but a variable amount of perchloric acid. The points on lines 2090 show the duration of the incubation period and the total reaction time for the respective experiments. It will be seen that the rates were inversely proportional to the concentration of the acid.

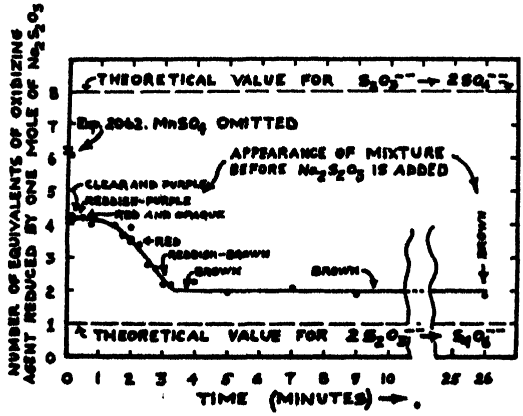

Fig. 1. First Evidence of the Autocatalytic Nature of the Guyard Reaction

The oxidation of sodium thiosulfate by a large excess of a mixture containing 0.00333 *M* potassium permanganate, 0.00867 *M* manganous sulfate, and 0.0667 *M* sulfuric acid, as a function of the age of the mixture. The figure also shows the appearance of the Guyard mixture, as a function of time.

The effect of sulfuric acid is less simple. The color change and the complete disappearance of permanganate ion take place earlier than in an equal concentration of perchloric acid. Sulfate ion tends to form a red complex with manganic ion. It will be shown in the theoretical part of this paper why this tendency exerts a strong influence on the course of the Guyard reaction. At this time it will suffice to state that the complex contains more than one sulfate radical, and for this reason the sulfate effect predominates over the acid effect at the higher concentrations of sulfuric acid. As a result, curve 2083 is bent toward the horizontal axis.

B-III. The effect of fluoride ion on the Guyard reaction. In series 2085 (figure 3) the concentration of potassium fluoride was the only variable. Fluoride ion forms a much more stable manganic complex than sulfate ion does. On the other hand, the color of manganic fluoride complex is not so pronounced that a small amount of it could be detected in the presence of a large amount of permanganate. Since fluoride ion also retards the precipitation of manganese dioxide, the net result is that small amounts of fluoride *appear* to increase the incubation period (the time at the end of which the solution begins to differ in appearance from a standard permanganate solution). When large amounts of fluoride are used, the consumption of

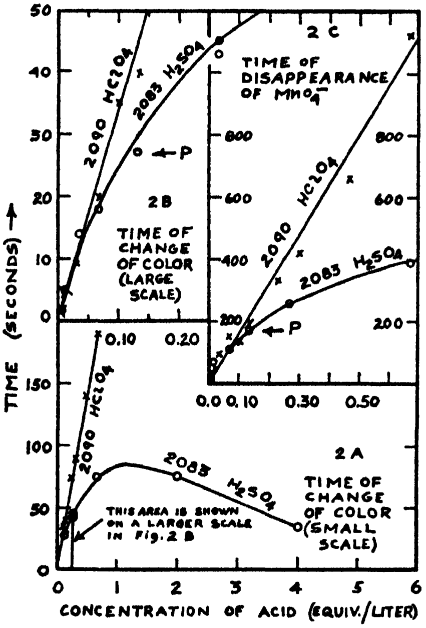

Fig. 2

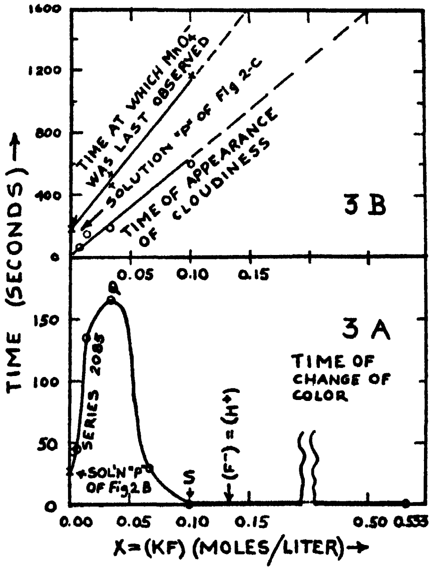

Fig. 3

Fig. 2. Time–Color Observations on Solutions Containing 0.00333 *M* Potassium Permanganate, 0.00835 *M* Manganous Sulfate, and Varying Concentrations of Perchloric or Sulfuric Acid

The incubation period, preceding the change of color toward red, is shown in figures 2A and 2B. The total reaction time is shown in figure 2C. The precipitate appears soon after the color begins to change.

Fig. 3. The Incubation Period, the Time of Appearance of the Precipitate, and the Total Reaction Time in Solutions Containing 0.00333 *M* Potassium Permanganate, 0.00835 *M* Manganous Sulfate, 0.133 *N* Sulfuric Acid, and Varying Amounts of Potassium Fluoride

In the ascending branch of curve 2085 the accelerating effect of the fluoride ion is masked by the retardation of the precipitation of manganese dioxide.

permanganate manifests itself in a weakening of the purple color. Under such conditions it becomes obvious that fluoride ion speedily converts permanganate and manganous ion into manganic fluoride complex (descending part of curve 2085). The precipitation of manganese dioxide is progressively retarded by increasing amounts of fluoride ion (figure 3B).

It will be recalled that fluoride ion combines with hydrogen ion, forming a weak acid. This is a factor which should be taken into consideration when interpreting curve 2085. A vertical arrow indicates the concentration of fluoride which is equivalent to the acid present. It is obvious that a rapid color change takes place even in solutions in which not all the hydrogen ion was used up by the fluoride.

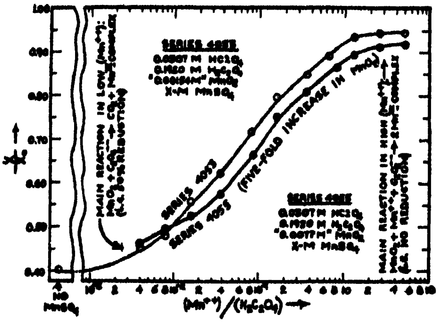

Fig. 4

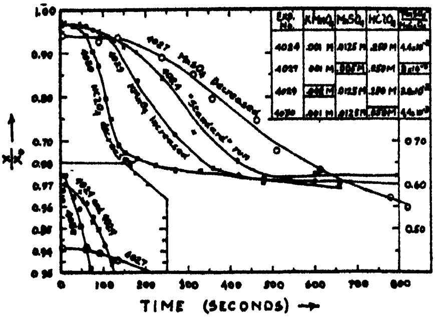

Fig. 5

Fig. 4. The Influence of Manganous Ion on the Manganese Dioxide–Oxalic Acid Reaction

X/X_0 is the ratio of the number of equivalents of manganic ion formed to the number of equivalents of manganese dioxide used. In the absence of manganous ion the reaction can follow only one path. In the presence of manganous ion the reaction can follow two paths. When the ratio $(Mn^{++})/(H_2C_2O_4)$ is large, the second path predominates. The extreme limits of the curve fall below the theoretical values 0.50 and 1.00 because of induced oxidation of oxalic acid.

Fig. 5. The Effect of Perchloric Acid, Potassium Permanganate, and Manganous Sulfate on the Course of the Guyard Reaction

X/X_0 gives a measure of the amount of manganese dioxide formed. The lower left insert shows the initial portions of the four curves, with a larger vertical scale. The upper right insert gives the initial concentrations in the four solutions. The last column gives the value, toward the end of each run, of the ratio which determines the final titer value of the solution (cf. figure 4).

B-IV. The reaction of manganese dioxide with oxalic acid. A semi-quantitative method of analyzing a changing Guyard mixture. Curves 4053 and 4055, figure 4, show the results of two series of experiments in each of which known quantities of freshly precipitated manganese dioxide were treated with solutions containing the same amount of oxalic acid and varying amounts of manganous sulfate. The oxalic acid was immediately followed with potassium iodide. It is obvious from figure 4 that at low concentrations of manganous ion the manganese dioxide dissolves by oxidizing the oxalic acid. At high concentrations of manganous sulfate the manganese dioxide dissolves without an appreciable loss of oxidizing titer, by oxidizing the manganous ion. It follows that oxalic acid can be used to differentiate between manganese dioxide and permanganate ion only in those solutions in which the concentration of manganous ion is not too large (see section A–IV).

B–V. The effects of acid, of permanganate ion, and of manganous ion on the course of the Guyard reaction. The course of the Guyard reaction, as revealed by the oxalic acid method, is shown in curve 4024, figure 5. The initial composition of the solution is given in the figure. At the desired time the reaction was stopped by adding excess oxalic acid. This was followed at once with potassium iodide. The loss of oxidizing titer gave a measure of the amount of manganese dioxide formed. Each point on the curve represents one such experiment. The other three curves in figure 5 show the effects of acid, of permanganate ion, and of manganous ion. A decrease in the acid concentration or an increase in the concentration of either one of the two reacting ions increases the rate of the Guyard reaction.

In a separate series of experiments it was found that direct sunlight has only a small effect, if any, on the rate of the reaction.

B–VI. Manganese dioxide catalyzes the Guyard reaction in acid solution. Curve 4042, figure 6, shows the usual course of the Guyard reaction in a solution whose composition is the same as in series 4030, figure 5. In series 4043, 10 per cent of the permanganate had been converted into manganese dioxide before the acid and the remainder of the manganous ion were added. In calculating the loss of oxidizing titer, allowance was made for the fact that manganese dioxide was present to start with. The catalytic effect is pronounced.

The manganese dioxide used as initial catalyst in series 4043 was prepared in neutral solution. As shown in figure 6, the effectiveness of the catalyst did not change on "aging" it either in neutral or in acid solution. Curves 4046 and 4050 show that the activity of manganese dioxide prepared in acid solution is smaller. Visual observations on the color and the rate of settling of the precipitate gave convincing evidence that the "neutral" solid was more highly dispersed than the "acid" one. Once the solid had formed, its degree of dispersion was affected only very little by aging it either in neutral or in acid solution.

B–VII. The chemical composition of the solid used as catalyst. Since the catalytic activities of the "acid" and the "neutral" catalysts differed so markedly, the solids were analyzed to determine the valence of the manganese in each. In preparing the catalyst, a small amount of manganous ion was added to excess permanganate. The composition of the solid was determined iodometrically; the heterogeneous mixture was filtered, and the distribution of oxidizing titer between precipitate and filtrate was studied. The following results were obtained (see figure 7).

Experiment 4061. Catalyst was prepared in acid solution. The reagents were introduced into a flask in the indicated order: 10.0 cc. of 0.002 *M* potassium permanganate; 1.0 cc. of 1 *M* perchloric acid; 0.30 cc. of 0.01 *M* manganous sulfate. Theoretical distribution of oxidizing titer, if manganese dioxide is formed: 10 per cent in the solid phase, 90 per cent in the precipitate. Theoretical distribution if manganic oxide (Mn_2O_3) is formed: 3.75 per cent and 96.25 per cent. Observed distribution: 10.3 per cent and 87.0 per cent.

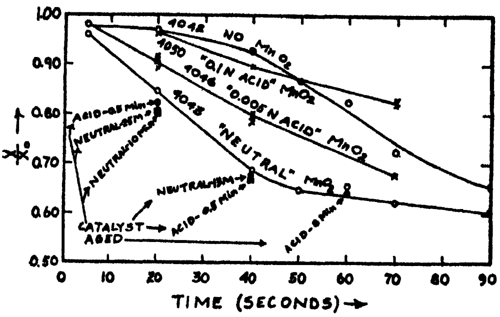

FIG. 6

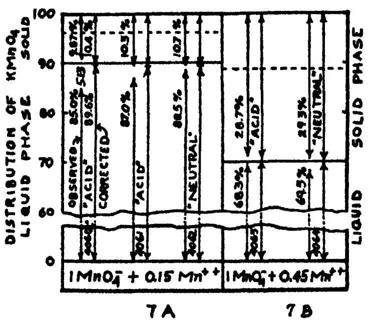

FIG. 7

FIG. 6. THE CATALYTIC EFFECT OF MANGANESE DIOXIDE IN THE GUYARD REACTION IN ACID SOLUTION

Manganese dioxide prepared in neutral solution is more active than that prepared in acid solution. "Aging" the catalyst, either in neutral or in acid solution, does not affect its activity. This is due to the fact that the highly dispersed "neutral" manganese dioxide does not coagulate into larger particles on acidulation.

FIG. 7. THE CHEMICAL COMPOSITION OF THE CATALYST

The solid horizontal lines indicate the theoretical titer distribution between the liquid and the solid phase if the catalyst is MnO_2. The dotted lines give the theoretical distribution if the catalyst is Mn_2O_3. The experimental values were corrected by the same factor, to add up to 100%. It is obvious that the manganese in the catalyst is tetravalent.

Experiment 4062. "Neutral" catalyst was prepared (perchloric acid omitted). Observed distribution: 10.6 per cent and 88.5 per cent.

In experiments 4061 and 4062 the same procedure was used as had been previously used in experiments 4050 and 4043, of figure 6. In the following two experiments the amount of manganous sulfate added was increased threefold. In these two experiments the theoretical distributions for manganese dioxide and manganic oxide are, respectively, 30 to 70 per cent and 11.25 to 88.75 per cent.

Experiment 4064. "Acid" catalyst was prepared. Observed distribution: 29.3 per cent and 68.3 per cent.

Experiment 4065. "Neutral" catalyst was prepared. Observed distribution: 28.7 per cent and 69.5 per cent.

The experimental results show that both in the "acid" and in the "neutral" catalyst the manganese was tetravalent. Thus, it is highly probable that the difference in catalytic activity was due entirely to the difference in surface exposed.

DISCUSSION OF RESULTS

In the light of recent evidence on the equilibrium existing in an acid mixture containing permanganate and manganous ions (2), it is possible to give a tentative explanation of the experimental results described in this paper. In an acid mixture of manganous and permanganate ions a *rapid* equilibrium is established, in which the concentrations of Mn^{+++} and of Mn^{++++} are extremely small. The tetravalent ion hydrolyzes, forming a hydrate of manganese dioxide. The formation of the precipitate is slow; it takes a measurable time before the presence of the solid changes the color of the solution, hence the incubation period. The solid catalyzes the further precipitation of manganese dioxide. The effect of the acid is due partly to its influence on the degree of dispersion of the solid and partly to some other, as yet unknown, influence.

The complex-forming sulfate ion modifies the reaction by shifting the equilibrium and directing the reaction through a new path, involving the manganic sulfate complex. Fluoride ion has a more pronounced effect because it forms a more stable complex.

The immeasurably fast rate of the reaction taking place when oxalic acid is added to an acid mixture of manganous and permanganate ions is due to the rapid formation of manganic oxalate ion and the resulting rapid shift of equilibrium. A more detailed discussion of this reaction will appear elsewhere (3).

In a mixture containing manganese dioxide, manganous ion, and oxalic acid two competitive reactions seem to take place. In one of these the oxalic acid merely forms manganic oxalate complex; in the other reaction the oxalic acid is oxidized. The data shown in figure 4 seem to indicate that the rates of these two reactions are of the same order of magnitude. At the present time it would be premature to speculate whether the competition is between the rates of formation of Mn^{++++} and of Mn^{+++} or between the rates of reaction of these two ions with oxalic acid.

Thiosulfate ion probably forms a manganic thiosulfate complex analogous to the red ferric thiosulfate complex. It is highly probable that thiosulfate ion, when added to an acid mixture of manganous and permanganate ions, shifts the equilibrium, forming manganic thiosulfate ion. The latter decomposes at once, forming manganous ion (early part of the curve shown in figure 1). If manganous ion is absent, as in experiment 2002, figure 1, the thiosulfate reacts with the permanganate by some other reaction path, and this results in a higher consumption of oxidizing agent. Thus, the apparently anomalous effect of manganous ion, discussed in section B–I, is probably due to this rapid shift of equilibrium.

SUMMARY

In acid solution the reaction between manganous and permanganate ions has an incubation period and is catalyzed by the manganese dioxide formed in the course of the reaction.

The rate of the reaction is increased by a decrease in the acidity or by an increase in the concentration of either the manganous or the permanganate ion.

Sunlight has only a small effect, if any, on the rate of the reaction.

The reaction can be accelerated by the addition of manganese dioxide to the initial solution. The catalyst prepared in a neutral solution is more effective than that prepared in acid solution. The difference is probably due to the larger degree of dispersion of the "neutral" manganese dioxide.

Sulfate and fluoride ions modify the reaction by carrying it through another path involving the intermediate formation of moderate amounts of the respective manganic complex ion.

Oxalate ion not only diverts the reaction rapidly into a new path, but also leads to the formation of entirely different reaction products.

When a solution containing both oxalic acid and manganous ion is added to freshly precipitated manganese dioxide, the amount of oxalic acid oxidized depends chiefly on the ratio: $(Mn^{++})/(H_2C_2O_4)$.

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ACTION OF RADON ON POLYMETHYLENES: CYCLOPENTANE AND CYCLOPENTENE

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In a previous paper (5) the action of radon on cyclopropane was reported. The study of the action of radon on this type of hydrocarbon was continued to permit comparisons of their behavior with that of the aliphatic hydrocarbons to be made and to study the relation of the values of the $-M/N$, the heats of formation, and the

$$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$$

The procedures and methods of calculation of the $-M/N$ values were those used in a previous paper (4). The results of the present work are summarized in the upper part of table 1. The lower figures are given for purposes of comparison.

A comparison of the values of $-M/N$ and

$$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC}$$

for cyclopentane with the corresponding values for the saturated aliphatics and those of cyclopentene with those of ethylene show a very striking similarity—in fact the values are practically identical.

In a previous paper (6) the writer pointed out the fact that the $-M/N$ values for compounds with positive heats of formation from diamond and hydrogen are low—ordinarily about 2. The values of $-M/N$ for those compounds whose heat of formation was negative were larger than 2, and the values increased with the increase of the negative heat of formation. The heat of formation of cyclopentane from diamond and hydrogen was calculated from the heat of combustion by means of the general expression

$$m\mathrm{C}_{\mathrm{diamond}} + \frac{n}{2}\mathrm{H}_2 \rightarrow \mathrm{C}_m\mathrm{H}_n + 92.1\,m + 34.2\,n - \text{heat of combustion}$$

The heat of combustion of cyclopentane is 783.6 (9), and the heat of formation is 18.9 kg-cal. The value of the $-M/N$ is 1.7. The heat of combustion of cyclopentene has not been determined experimentally, but was calculated by the method of Kharasch (10) and was found to be 735.9. The heat of formation from hydrogen and diamond based on this value is -1.8 kg-cal., and the $-M/N$ is 4.5. The correlation of these values of the heats of formation and the $-M/N$ is very satisfactory.

Inasmuch as very pure samples of these substances were available, their vapor pressures were determined.

TABLE 1

Summary of results

HYDROCARBON	$-\Delta P_{HC}$ IN MM.	PER CENT $-\Delta P$ USED IN CALCULATION	$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$	$-M/N$	HEAT OF FORMATION (DIAMOND $+ H_2$)	PRODUCT
Cyclopentane .	32.9	100	73 7	1 7	18.9	Light colored mobile liquids
Cyclopentene...	91.0	97 0	19 2	4 5	−1 8	
Methane........			75 7	2 2	20 4†	
Ethane........			91 1	1.7	25 5	Light colored liquids
Propane........			82.3	1.7	30 3	
Ethylene........			16.0*	4 8	−6.4	

* During the first part of the reaction. The ratio increases, owing to action on the product.

† Calculated from heats of combustion given in International Critical Tables Vol. V, p. 163 (1929).

EXPERIMENTAL

Preparation of cyclopentane

This substance was prepared by the reduction of (a) cyclopentadiene and (b) cyclopentene in an Adams hydrogenation apparatus using a platinum oxide catalyst. Since these methods of preparation have not been previously described, they are given in some detail.

Dicyclopentadiene (60 cc.) was depolymerized by heating the polymer in a Clarke flask contained in a metal bath at 185°C. The temperature was gradually increased to 215°C. at the end of the process. Thirty cc. of cyclopentadiene dissolved in 175 cc. of 95 per cent ethanol to which 0.5 g. of platinum oxide catalyst (prepared according to the directions in Organic Syntheses, Vol. VIII, p. 92) were reduced in the Adams hydrogenation apparatus. Only 80 per cent of the calculated amount of hydrogen was taken up. The portion distilling to 78°C., but chiefly between 40–45°C., was thoroughly agitated successively with water, concentrated sulfuric acid, and dilute sodium hydroxide, and then dried over fused calcium chloride. The sample distilled between 49–50°C. On treating the alcohol used as a solvent with water, an oily solid separated which was identified as tetrahydrodicyclopentadiene by its melting point. This compound had been described by Eijkman (1). Its formation undoubtedly accounts for the low absorption of hydrogen.

Forty cc. of cyclopentene dissolved in 150 cc. of ethanol was hydrogenated using 0.25 g. of the oxide catalyst. The calculated amount of hydrogen was absorbed in about an hour. The product was removed by distilling at 78°C. and was purified as described previously. Any traces of unsaturated impurity were removed by thoroughly agitating with an alkaline permanganate solution until a portion did not decolorize a very dilute solution. After drying over calcium chloride, the sample distilled at 48.8°C. at 738.4 mm. The boiling point at 760 mm. was calculated to be 49.6°C. (3). The boiling point given in the International Critical Tables is 49.5°C. (8).

Purification of cyclopentane

The cyclopentane prepared from the cyclopentene was held over bright sodium under its own vapor. Fresh sodium was used each day. The surface was not coated after standing thirty-six hours. The sample was distilled three times under its own vapor pressure from a trap maintained at 0°C. and condensed in a trap at −80°C. The vapor pressure was 107.3 mm. at 0°C. and was unchanged by the distillations. After two distillations from −20°C. to a trap at −80°C. the vapor pressure at 0°C. was 107.3 mm. The vapor pressure of the first fraction and of the last fraction at 0°C. was 107.3 mm.

Action with radon

Very shortly after mixing the cyclopentene with radon a fog appeared. The product collected as a mobile nearly colorless oil on the bottom of the reaction sphere, and was not appreciably affected by further action of radon as shown by the constancy of the ratio

$$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$$

Typical data is given in table 2.

Preparation of cyclopentene

Cyclopentene was prepared by the dehydration of cyclopentanol by heating with hydrated oxalic acid. The cyclopentanol was made by the reduction of cyclopentanone, using a Raney nickel catalyst and hydrogen under high pressure. Cyclopentanone (148.5 g. or 1.77 moles) from the Eastman Kodak Co. was reduced with hydrogen at an initial pressure of 1600 lbs., using 8 g. of Raney nickel catalyst but no solvent. After four hours at 150°C., 90 per cent of the calculated amount of hydrogen was absorbed. The contents of the bomb were filtered through a sintered glass crucible, and the residue was washed with a little absolute alcohol. The filtrate was distilled through a Widmer column with an electrically heated jacket. An oil bath was used to heat the sample. The following fractions were collected.

TABLE 2

Polymerization of cyclopentene by alpha rays from radon

$C_5H_8 \rightarrow$ liquid. Temp. 25°C.; is = 3.95; i = 1.23; s = 3.21. Reaction sphere: volume = 35.309 cc.; diameter = 4.070 cm.; E_0 = 0.03395 Curie

TIME		RADON	PRESSURE			$\Delta P_{H_2 + CH_4}$	$\frac{\Delta(H_2+CH_4)}{-\Delta C_5H_8} \times 100$	ku/λ	$-M/N$
Days	Hours		Total	C_5H_8	$H_2 + CH_4$				
		per cent	*mm.*	*mm.*	*mm*				
		100.000	168.7	168 7					
	1 03	99.231	166.9	163 9				40 5	5 0
	3.15	97 665	163 6	163 6				37 7	4.7
	7.18	94 757	158.3	152 3	1 0	1 0	15 9	39 9	4 9
	9 32	93.260	155 6	154 3	1 3	0.3	10 00	37 6	4 7
	14.6	89 629	149 3	147 3	2 0	0.7	10 00	37.7	4.7
	23 65	83 747	140 0	136.3	3 7	1 7	15 45	38 9	4.8
1	3.57	81 311	137 0	132.8	4 2	0 5	14 26	31 5	3 9
1	9 40	77 832	132 4	126 4	6 0	1.8	28.08	41 7	5 2
1	12 73	75.928	129.8	123 1	6 7	0 7	21.20	41 0	5 1
2	0.23	69.648	122.9	114 2	8 7	1.0	11 24	35 2	4 4
2	5.23	67.086	120.2	110.8	9 4	0.7	22.90	34.9	4 4
3	1.38	59.679	111 8	100.0	11 8	2.4	26.10	32 1	4.2
3	5.98	55.719	110.3	97.9	12 4	0.6	28 60	31.8	4.0
4	9.11	45.461	103.0	88.3	14 7	2 3	23.99	29 6	3 7
5	0.37	40.546	99 9	83.8	16.1	1.4	31.10	31 5	4.0
6	0.10	33.935	96.1	77.7	18 4	2.3	37 64	33.6	4 2
6	8.15	31.947	94 8	75 1	19.7	1.3		50.5	6 3
Weighted average							19.15		4.5

Fraction I	77–78°C.	Solvent discarded
Fraction II	135–136°C.	Discarded
Fraction III	136–137.5°C.	Collected
Fraction IV	Above 137.5°C.	Discarded

Fraction III weighed 134.7 g. and 95 per cent of it boiled between 137–137.5°C. The yield was 91 per cent.

The reduction of cyclopentanone to the cyclopentanol has also been carried out by Godchot and Tabourg (2). They obtained some unreacted cyclopentanone, cyclopentane, 50 per cent of the weight of the starting substance as cyclopentanol, and 40 per cent as a ketone having the formula $C_{10}H_{16}O$.

Cyclopentanol (110 g. or 1.17 moles) and 600 g. of hydrated oxalic acid (4.8 moles) were placed in a 1-liter Claisen flask. The flask was heated in a Wood's metal bath until the contents began to liquefy. A condensate began to appear in the condenser when the temperature of the mixture was 80°C. The heating was then gradually increased until no more solid was present (110°C.), and held at that temperature for 30 minutes. The temperature of the distillate gradually increased to 80°C. The temperature of the metal bath was increased until the temperature of the vapors distilling was 100°C. Very soon after this temperature was reached, the condensate was clear, indicating that no more product was being obtained; the heating was then stopped. The time of heating was about two hours.

The cyclopentane was separated from the aqueous layer and dried over calcium chloride. The crude material weighed 55.5 g., making a yield of 70 per cent. The dried product was then distilled from sodium. The distillation started at 43°C. and the temperature quickly rose to 43.8°C. When the temperature reached 45.5°C. the distillation was stopped. The 49.0 g. of the product (62 per cent yield) was mixed with the products obtained in preliminary runs, and allowed to stand overnight over sodium. On distilling, the material boiled between 43.5°C. and 43.8°C. A small fraction boiling between 43.8°C. and 44.1°C. was also obtained. The barometric pressure was about 740 mm.

In order to dry it thoroughly and to remove any trace of unchanged cyclopentanol, a portion of the material was placed in a vessel previously filled with dry nitrogen containing bright pieces of sodium; after freezing in liquid oxygen the nitrogen was pumped off. After standing twelve hours under its own vapor at 0°C. a brown sludge was formed; the sample was then distilled at low temperatures into a second evacuated vessel containing a few pieces of bright sodium. After remaining three days in contact with the sodium no sludge was formed and the surface of the sodium was bright.

Purification of cyclopentene

The sample was then distilled from a trap maintained at 0°C. and was condensed at −182°C. The first and last 1.5 cc. were discarded. A second distillation was made from 0°C., and condensation took place at −182°C. Then the sample was cooled to −182°C. and any non-condensable gases were pumped off. The temperature was raised to 0°C. and, after cooling, the pumping operation was repeated to remove any residual non-condensed gas. The vapor pressure of the sample at 0°C. was 131 mm. The sample was then distilled two times from −30°C. to −182°C. When two-thirds of the sample had distilled, the vapor pressure of the residue was found to be 131 mm. at 0°C. A second distillation under the same conditions was carried out. The vapor pressure of the low-boiling fraction was

131 mm. at 0°C. The vapor pressure of the middle sample was also 131 mm. at 0°C. A sample to use in determining the vapor pressure at various temperatures and to subject to the action of α-particles was taken, after about a third of the material had been distilled off. The vapor pressure of this sample was 131 mm. at 0°C.

TABLE 3

Polymerization of cyclopentane by alpha rays from radon

C_5H_{10} gas → liquid. Temp. 25°C.; $is = 4.3$; $i = 1.24$; $s = 3.48$. Reaction sphere: volume = 35.805 cc.; diameter = 2.045 cm.; $E_0 = 0.03718$ Curie

TIME		RADON	PRESSURE			$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta P_{C_5H_{10}}}$	$k\mu/\lambda$	$-M/N$
Days	Hours		Total	C_5H_{10}	$H_2 + CH_4$			
		per cent	*mm.*	*mm.*	*mm.*			
		100.000	105.5					
	2.22	98.364	105.5	105.2	0.3	100.0	4.9	0.6
	4.08	96.987	105.5	104.6	0.9	100.0	11.2	1.3
	7.22	94.729	104.9	103.2	1.7	57.2	15.9	1.8
	9.83	92.892	104.6	101.9	2.7	77.0	18.5	2.1
	22.90	84.219	103.2	97.2	6.0	70.3	14.7	1.7
1	1.77	82.426	103.0	96.0	7.0	83.3	18.7	2.2
1	19.33	72.253	101.5	90.8	10.7	64.8	14.2	1.7
2	9.58	64.931	101.0	87.7	13.3	83.8	12.8	1.5
2	20.75	59.715	100.4	85.7	14.7	70.0	11.9	1.3
3	8.56	54.653	100.1	83.1	17.0	88.5	16.3	1.9
4	4.20	47.168	99.3	79.3	20.0	78.8	16.8	1.9
4	18.8	42.276	99.1	77.8	21.3	86.7	16.2	1.9
7	19.8	24.450	98.0	72.3	25.7	79.9	11.3	1.3
Weighted average..............................						73.7		1.7

TABLE 4

Vapor pressures of cyclopentane and cyclopentene

t	VAPOR PRESSURE OF CYCLOPENTANE	t	VAPOR PRESSURE OF CYCLOPENTENE
°C.	*mm.*	*°C.*	*mm.*
−52.0	4.4	−77.5	1.0
−47.5	6.1	−50.8	6.1
−38.8	12.1	−26.8	31.0
−25.9	27.3	−9.2	81.9
−14.4	53.0	0.0	129.3
0.0	107.4	+6.8	178.1
6.0	140.7	+12.3	226.6
13.6	197.6	15.0	253.1
18.4	241.8	19.9	309.4
		43.5	731.2

Action with radon

The action with radon was practically identical with that of cyclopentane. The data is given in table 3.

Vapor pressures

The vapor pressures of cyclopentane and cyclopentene at various temperatures were determined using the method and apparatus previously described (7). The results are given in table 4.

SUMMARY

1. Pure cyclopentane and cyclopentene have been prepared, and the vapor pressures at several temperatures have been determined.

2. The action of radon on these compounds has been studied. The $-M/N$ values are in agreement with the heats of formation and with

$$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC}$$

The writer wishes to acknowledge the grant from the Graduate School to aid in carrying out this work and the assistance of Lucille M. Heisig in determining the vapor pressures.

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ELECTROMETRIC AND ANALYTICAL EVIDENCE FOR THE COMPOSITION OF PRECIPITATED BASIC COPPER PERCHLORATE

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The composition of the precipitate formed when carbonate-free alkali is added to solutions of copper salts can be estimated, without analysis, by electrometric titration, using the quinhydrone electrode as pH indicator. The application of the method to several copper salts has been previously described (1, 6). In all cases where evidence was obtained for a definite basic salt, the composition was that of the 1:3 salt, for example, $CuCl_2 \cdot 3CuO \cdot (?)H_2O$. Such 1:3 precipitates have been formed under favorable conditions from solutions of the following copper salts: sulfate, chloride, nitrate, and trichloroacetate.

To extend the list further, the precipitation of basic copper perchlorate has been studied by the electrometric method. Unlike the cases previously investigated a 1:6 salt is formed, i.e., $Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O$. Because of this anomalous behavior, the composition of the precipitated basic salt has been tested further by direct analysis for the copper to perchlorate ratio. The results confirm the formula derived by the electrometric method.

EXPERIMENTAL

Preparation of solutions

A solution of carbonate-free sodium hydroxide was prepared by the method of Cornog (5).

Copper perchlorate solutions were made by two methods. For solution A, barium chloride was added in slight excess to a solution of copper sulfate, and the precipitated barium sulfate was removed by centrifuging. A small weighed excess of perchloric acid was added to prevent hydrolysis. In making solution B, an excess of vacuum-distilled perchloric acid was allowed to react with basic copper carbonate. Aside from the excess acid, this solution contained only copper and perchlorate ions. The acid present was estimated by the position of the initial breaks in the curves, as shown in figure 1 (7). Both solutions were standardized for copper content by the iodometric method. A blank test showing no liberation of iodine from potassium iodide by perchlorate ion in weak acid solution demonstrated that the method was applicable.

Electrometric titrations

Both direct and delayed titrations were used as previously described in the case of copper trichloroacetate (1). Using a saturated calomel reference electrode, an E.M.F. value of + 0.007 volt was chosen as the end-point, this being the point of maximum slope of the titration curves. In all of the titrations of solutions of initial concentration greater than 0.1 *N*, very nearly 1.714 moles of alkali were required per mole of copper salt. This indicates a 1:6 basic salt.[1] The results for the direct titrations are shown

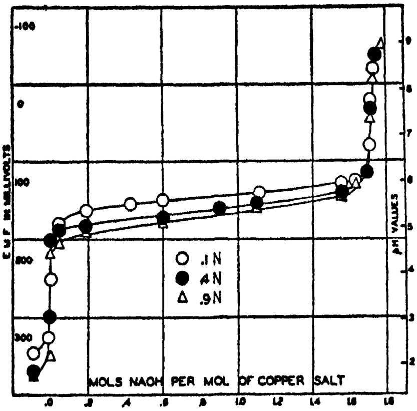

FIG. 1

TABLE 1

Use of direct titrations in determination of alkali required per mole of copper perchlorate

(1.7143 required for 1:6 basic salt)

SOLUTION A		SOLUTION B	
Normality of copper perchlorate solution	Moles of NaOH	Normality of copper perchlorate solution	Moles of NaOH
1.000	1.710	1.000	1.713
0.400	1.714	0.400	1.714
0.266	1.714	0.100	1.715
0.100	1.711		

---

[1] According to the equation, $7Cu(ClO_4)_2 + 12NaOH = Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O + 6Na_2SO_4$, the ratio of moles of sodium hydroxide to moles of copper salt is 1.7143:1.

in figure 1 and table 1;[2] those for the delayed titrations, in table 2. In the delayed titrations it is certain that sufficient time was allowed to let the system come to equilibrium. Because the results were identical for the direct and the delayed titrations, it may be concluded that the precipitates were in equilibrium with the solutions even in the direct titrations.

For solutions less concentrated than 0.1 *N*, more than 1.714 moles of alkali were required. This indicates that under these conditions the precipitate was probably a mixture of the 1:6 salt and hydrated copper oxide.

TABLE 2

Use of delayed titrations in determination of alkali required per mole of copper perchlorate

SOLUTION OF $Cu(ClO_4)_2$ USED	NORMALITY OF $(CuClO_4)_2$	TIME OF STANDING	TREATMENT	MOLES NaOH ADDED INITIALLY	TOTAL MOLES NaOH
A	0.10	20 hours	a*	1.633	1.712
A	0.10	20 hours	b†	1.633	1.712
A	0.10	8 days	b	1.626	1.711
A	0.27	20 hours	a	1.636	1.711
A	0.27	20 hours	b	1.633	1.711
A	0.27	8 days	b	1.633	1.712
B	0.40	20 hours	a	1.557	1.714
B	0.40	20 hours	b	1.557	1.714
B	0.40	8 days	b	1.557	1.714
B	0.10	20 hours	a	1.557	1.715
B	0.10	20 hours	b	1.557	1.716
B	0.10	8 days	b	1.557	1.715
B	0.93	20 hours	a	1.557	1.714
B	0.93	20 hours	b	1.557	1.713
B	0.93	8 days	b	1.557	1.714

* a denotes constant stirring.
† b denotes occasional shaking.

Analysis of the precipitate

To 0.4 *N* copper perchlorate, alkali was added in amounts somewhat less than 1.714 moles per mole of copper salt.[3] After three washings by centrifuging and decantation, the moist precipitate was dissolved in dilute sulfuric acid to make a stock solution. Separate aliquot portions of this solution were analyzed for copper iodometrically, and for perchlorate by the nitron method (4). In the basic salt $Cu(ClO_4)_2 \cdot 3CuO \cdot (?)H_2O$, the ratio of moles of copper to moles of the perchlorate radical should be 7:2. Analysis of one precipitate from copper perchlorate solution A yielded a ratio of 6.96:2. Two precipitates from solution B each yielded a ratio of 6.99:2.

---

[2] Points on the curves above pH 7, approximately, do not represent equilibrium conditions. On standing a rather rapid decrease in pH is observed, owing to the interaction of the excess hydroxyl ions with the precipitated basic salt.

[3] More than 1.7143 moles of alkali would, of course, convert a part of the basic salt into hydrated copper oxide, so that the precipitate would not have definite composition.

DISCUSSION

Previously both electrometric (1, 6) and phase rule studies (2) have established the individualities of several 1:3 basic salts of copper of which $CuSO_4 \cdot 3CuO \cdot 4H_2O$ is an example. Britton (3) has given a review of the various theories, based on constitution, which have been proposed to account for this regularity of behavior. Now, with definite evidence for a 1:6 basic copper perchlorate, any future theories must explain the structure of this salt as well. The authors believe that no satisfactory theory has yet been advanced.

SUMMARY

1. When alkali is added to an excess of copper perchlorate in solutions above 0.1 *N*, the precipitate has the constitution: $Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O$. This compound has not been reported in the literature.

2. This 1:6 salt is unlike any other basic salts of copper previously known.

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SOLUBILITY OF SEVERAL COMPOUNDS OF THE MANNOSE SERIES IN ALCOHOLS

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INTRODUCTION

This investigation records solubilities of *l*-rhamnose, α-*d*-mannose, β-*d*-mannose, *d*-mannonic-γ-lactone, *d*-mannonic-δ-lactone, α-methyl-*d*-mannoside, and *d*-mannitol in methyl, ethyl, allyl, propyl, isopropyl, and the four isomeric butyl alcohols. An attempt has been made to compare the solvent properties of this series of alcohols for a given sugar, and in addition to compare the effect of structure of the sugar derivatives on solubility in a given solvent. Practically no data of this kind are now available. The results of Creighton and Klauder (4) for the solubility of mannitol in ethyl alcohol at 60°C. do not agree with those presented here, since they report mannitol as much more soluble than we have found it to be.

EXPERIMENTAL

Materials

l-Rhamnose hydrate was purified by recrystallization from methyl alcohol, m.p. 92°C., $[\alpha]_D^{20°} = -7.7°$ (initial) and $+8.85°$ (final). α-*d*-Mannose was obtained according to the method of Levene (6), m.p. 132–135°C., and β-*d*-mannose was obtained according to the method of Riiber and Minsaas (7). Its constants were m.p. 133.5°C., $[\alpha]_D^{20°} = -18°$ (initial) and $+14.6°$ (final). The constants for the *d*-mannonic-γ-lactone were m.p. 152°C. and $[\alpha]_D^{20°} = +52.3°$ with no change in twenty-four hours. For the *d*-mannonic δ-lactone, m.p. 162.5°C., $[\alpha]_D^{20°} = +112°$ two minutes after solution. α-Methyl-*d*-mannoside had a melting point of 195°C. and a rotation $[\alpha]_D^{20°} = +80.6°$. *d*-Mannitol melted at 167°C. and its rotation $[\alpha]_D^{20°} = +24.5°$ in the presence of borax.

The physical constants as above given established the purity of the different solutes used.

Each of the alcohol solvents was purified by means of a prolonged drying process with calcium oxide and was then subjected to careful fractionation, using an efficient fractionating column. The fractions selected corresponded very closely in boiling point and density with the best values recorded in the literature. These constants are summarized in table 1.

Procedure

The solubility determinations were made by the synthetic method of Alexejew (1). Among the other workers who have used the method are Carrick (2), Collett and Johnston (3), Kendall and his students (5), Schroder (8), Sidgwick and his students (9), Sunier (10), and Ward (11).

TABLE 1

Summary of constants for alcohols

ALCOHOL	BOILING TEMPERATURE (CORRECTED)		DENSITY IN GRAMS PER CC. AT 20°C.	
	Found	Accepted	Found	Accepted
	°C.	*°C.*		
Methyl	65.2	64.5	0.7916	0.7917
Ethyl	78.6	78.5	0.7883	0.7893
Allyl	96.4–96.6	97.0	0.8530	0.855
Propyl (normal)	97.5–97.7	97.8	0.8034	0.804
Propyl (iso)	82.4	82.3	0.7853	0.7854
Butyl (normal)	117.5	117.7	0.8093	0.810
Butyl (secondary)	99.4–100.0	99.5	0.8067	0.808
Butyl (iso)	107.7–107.9	107.3	0.8016	0.802
Butyl (tertiary)*	82.5–82.6	82.8	0.7810†	0.781†

* Melting temperature = 24°C.

† At 25°C.

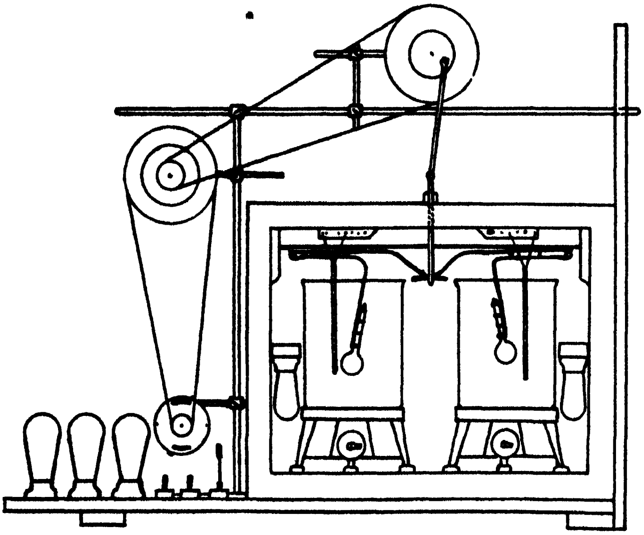

FIG. 1. THE APPARATUS

The essential feature of this method is to ascertain the temperature at which the last crystal just disappears when a known mixture of solvent and solute is slowly heated. Collett and Johnston (3) checked this method in comparison with the usual analytical method and found very good agreement between the two.

Small glass bulbs of 3 to 15 ml. capacity similar to those described by Collett and Johnston (3) were used, and their technique was followed in filling the bulbs and obtaining the weight of solvent and solute.

TABLE 2

Solubility in methyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
35.9	16.7	41 5	1.84	35.8	0.235
42 6	24 4	45 0	2 19	45.3	0.341
49.1	35 5	51.3	2 82	50.4	0.415
53 3	44.0	55 0	3 26	54.9	0.508
56 0	49.9	59.1	3 95	56.8	0 581
60.5	61.4	64.2	4 97	63.4	0.779
α-*d*-Mannose		*d*-Mannonic-γ-lactone		66 9	0.957
44.8	2.18	40.0	0.813	*d*-Mannitol	
46.1	2.29	47.9	1 083	47.0	0.0766
50.1	2 83	53 4	1 325	49.7	0.0874
50.2	2.84	60.9	1.797	60 8	0.136
53.9	3 38	67.4	2 367	66.0	0.173
58.9	4.22			69.7	0.210
62 6	5.07	α-Methyl-*d*-mannoside		72.9	0.256
		40.2	0 458	76 6	0 298
		43 7	0 523	77.3	0.316
		49.8	0 652	80 5	0.367
		54 9	0.776		
		58 4	0 867		
		62.4	1.010		
		64.6	1.094		
		66 8	1 205		

Figure 1 is a rough sketch of the apparatus used. The bath was a large beaker heated by means of an electric hot plate and filled with water for temperatures up to 95°C. and with paraffin oil for higher temperatures. Two determinations were made at one time. The bulbs were fastened to the shaker arms by means of rubber bands as indicated, and the whole was contained in a cabinet to reduce temperature variation to the minimum. The shaker arms made two hundred complete vibrations per minute; this was found to produce adequate stirring of the bath. Total immersion calibrated thermometers graduated in 0.2°C. intervals were used.

The temperature was raised fairly rapidly at first and then more slowly toward the end of a determination. The rate of heating could be controlled by the placing of one or more light bulbs in series with the heating elements. Usually approximately twenty minutes was required in raising the temperature the last degree. By means of the switch the shaking machine could be stopped momentarily for observation of the bulbs. The temperature recorded, as nearly as could be determined, was that point at which the last crystal of solute just disappeared. Usually two or three determinations of the solution temperature were made with each bulb. Recrystallization was carried out as rapidly as possible by cooling the bulbs

TABLE 3

Solubility in ethyl alcohol

TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		*d*-Mannonic-γ-lactone		*d*-Mannonic-δ-lactone	
42.0	7.93	44.1	0.207	42.0	0.0853
49.3	12.6	48.3	0.250	49.8	0.124
53.6	17.2	55.9	0.357	53.6	0.144
54.5	18.7	60.4	0.427	60.4	0.192
56.1	21.5	64.5	0.519	66.8	0.262
59.2	26.1			68.2	0.279
59.8	27.5	α-Methyl-*d*-mannoside			
59.9	27.9			*d*-Mannitol	
61.1	30.7	37.9	0.0940		
		47.4	0.177	53.6	0.0293
α-*d*-Mannose		48.5	0.186	62.0	0.0463
		52.4	0.229	63.3	0.0494
43.3	0.353	53.9	0.241	69.6	0.0634
52.0	0.490	54.6	0.247	73.0	0.0768
57.9	0.627	62.0	0.342	77.2	0.0989
58.3	0.639	66.1	0.413	80.3	0.122
61.1	0.695	76.2	0.615	85.2	0.166
67.6	0.895	81.0	0.761	92.5	0.255
		84.6	0.905		
β-*d*-Mannose					
48.2	0.337				
51.8	0.394				
55.3	0.455				
61.2	0.568				
65.4	0.697				
71.4	0.867				

in a refrigerator and shaking them by hand occasionally in order to obtain the solutes in the form of small crystals. Two careful determinations, the results of which showed a divergence not greater than 0.2°C., were considered satisfactory.

The determinations with *l*-rhamnose were difficult because the rather concentrated solutions were cloudy, and because rhamnose has a tendency to form large crystals. The usual time required to make the determination with either of the *d*-mannoses was three hours. Only one determination was made with each bulb, since the α- and β-*d*-mannose both undergo more or less mutarotation in alcohol solution and the recrystallized product is not a single substance. The two *d*-mannonic-lactones and the α-methyl-*d*-mannoside gave no difficulties. With *d*-mannitol initial determinations were not reliable, since it was found to recrystallize in one of two different

TABLE 4

Solubility in allyl alcohol

TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
35.8	4.05	47.2	0.235	42.0	0.0806
38.2	4.49	51.8	0.281	46.6	0.0964
46.1	6.28	55.5	0.338	53.0	0.127
49.2	7.58	58.4	0.392	57.7	0.156
54.5	10.72	65.0	0.511	62.0	0.192
59.8	14.90	68.2	0.586	67.6	0.247
60.5	15.62				
62.4	18.60	*d*-Mannonic-γ-lactone		*d*-Mannitol	
α-*d*-Mannose		46.4	0.215	55.9	0.0296
		49.7	0.250	59.4	0.0352
48.2	0.323	55.1	0.320	63.6	0.0460
52.0	0.378	60.4	0.404	69.3	0.0627
55.3	0.438	63.4	0.464	75.0	0.0854
56.5	0.455			79.7	0.112
66.6	0.672	α-Methyl-*d*-mannoside		84.7	0.141
		46.2	0.197		
		49.4	0.229		
		53.3	0.275		
		55.9	0.313		
		58.5	0.345		
		60.5	0.391		
		63.2	0.436		
		70.3	0.581		

TABLE 5

Solubility in n-propyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)	
31.0	2.43
40.0	3.32
41.3	3.61
46.1	4.43
51.2	6.04
56.5	8.04
61.1	10.33
63.2	12.44
α-*d*-Mannose	
41.3	0.129
47.1	0.164
56 4	0.248
60.0	0.290
63.1	0.320
68.4	0.396

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
β-*d*-Mannose	
48.7	0.123
53.0	0.149
59.8	0.192
65.6	0.250
70.3	0.306
75.7	0.419
d-Mannonic-*γ*-lactone	
42.2	0.0849
47.3	0.105
55.3	0.158
64.6	0 244
68 6	0.296
α-Methyl-*d*-mannoside	
45 8	0.077
48.9	0.099
54.6	0.148
60.1	0.194
68.1	0.270
75.3	0.386
86.5	0.622

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
d-Mannonic-*δ*-lactone	
45.9	0.0476
50.2	0.0566
53.9	0.0679
59.7	0.0945
65 4	0.123
71.4	0.157
d-Mannitol	
58.8	0.0193
61.5	0.0236
67.3	0.0328
73.7	0.0474
78.6	0.0631
89.2	0.108
90.9	0 122
97.7	0.174

TABLE 6

Solubility in isopropyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
36 8	3.01	47.1	0.130	45.6	0.0607
44 5	4.06	51.7	0.159	51.0	0.0748
49 3	5.37	58.3	0.206	55.4	0 0935
53 8	6.86	62.4	0 250	61.1	0.121
55 3	7.49	67.6	0.312	65.3	0.146
61 2	10.70	71.1	0.371	69.7	0.181
α-*d*-Mannose		*d*-Mannonic-γ-lactone		*d*-Mannitol	
40.2	0.131	43 8	0.109	55.2	0.0180
49.3	0 191	51 6	0.163	59.5	0.0224
52.3	0.227	57.4	0.215	65.7	0.0318
57 7	0.297	64 4	0.294	69.5	0.0459
59 3	0.321	67.9	0.349	79.3	0.0775
64 2	0.388	α-Methyl-*d*-mannoside		81.5	0.0882
		46.3	0.0876		
		51.6	0.129		
		57.3	0 164		
		60.8	0 206		
		65.7	0 254		
		68 0	0.276		
		73.8	0 362		
		79 7	0 486		

TABLE 7

Solubility in n-butyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
32.3	1.85	41.3	0.0679	48.1	0.0379
40.9	2.27	51.2	0.0815	50.8	0.0414
47.6	3.38	55.8	0.101	53.9	0.0472
53.6	4.39	60.1	0.127	59.6	0.0634
55.2	4.89	65.1	0.165	65.0	0.0822
61.0	6.66	72.6	0.245	69.4	0.103
α-*d*-Mannose		*d*-Mannonic-γ-lactone		*d*-Mannitol	
42.9	0.0888	47.1	0.0719	58.5	0.0131
47.1	0.101	51.3	0.0868	65.8	0.0199
51.0	0.116	54.7	0.106	67.1	0.0207
55.6	0.141	60.1	0.139	77.0	0.0407
55.8	0.142	63.0	0.163	84.2	0.0648
62.9	0.199	71.5	0.242	89.4	0.0887
69.6	0.281	α-Methyl-*d*-mannoside		95.2	0.1337
		45.8	0.0539		
		56.1	0.107		
		56.2	0.109		
		62.7	0.165		
		67.5	0.219		
		73.1	0.290		
		91.1	0.632		

TABLE 8

Solubility in secondary-butyl alcohol

TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
43.1	3.25	45.1	0.0933	44.9	0.0415
49.1	4.04	48.7	0.116	49.2	0.0487
51.8	4.53	53.9	0.144	54.0	0.0637
52.5	4.68	58.0	0.175	58.5	0.0827
58.6	6.41	65.2	0.239	64.9	0.115
65.4	8.74	70.6	0.301	71.9	0.152
72.4	13.86				
α-*d*-Mannose		*d*-Mannonic-γ-lactone		*d*-Mannitol	
		43.1	0.0807	53.5	0.0164
46.1	0.132	46.6	0.0927	60.3	0.0227
50.8	0.162	52.0	0.125	66.1	0.0286
55.4	0.199	57.4	0.167	69.5	0.0356
56.4	0.209	64.7	0.238	73.0	0.0432
64.0	0.281	68.7	0.286	83.3	0.0772
76.1	0.438			100.8	0.1904
		α-Methyl-*d*-mannoside			
		49.7	0.107		
		53.9	0.140		
		58.6	0.175		
		66.7	0.251		
		75.6	0.367		
		80.5	0.440		
		93.9	0.768		

TABLE 9

Solubility in isobutyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		*d*-Mannonic-γ-lactone		*d*-Mannonic-δ-lactone	
40.4	2.18	49.5	0.0659	46.8	0.0307
44.8	2.85	51.7	0.0770	52.3	0.0402
51.4	3.78	56 9	0.102	55.4	0.0461
55.0	4 51	63.3	0.142	59.5	0.0582
61.2	6.17	66.4	0.164	63.0	0.0693
66 6	7.83	75 1	0 236	68.1	0 0842
α-*d*-Mannose		α-Methyl-*d*-mannoside		*d*-Mannitol	
47.1	0.0848	46.1	0.0528	57.5	0.0110
52.1	0.102	51.1	0.0746	61.3	0 0149
55.1	0.118	56.0	0.104	67.4	0.0195
57.6	0.135	63.5	0.154	72.1	0.0269
62.6	0.180	69.4	0.221	73.6	0.0300
72.5	0.269	74.3	0.285	83.3	0.0538
		80.1	0.363	89.5	0.0754
β-*d*-Mannose		83.0	0.420	101.8	0 1636
47.0	0.0608				
49.8	0.0679				
54.0	0.0820				
58 2	0.103				
63.8	0.137				
72.1	0.203				

TABLE 10

Solubility in tertiary-butyl alcohol

TEMPERATURE IN °C	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
***l*-Rhamnose (hydrate)**	
42.4	3.97
53.2	5.99
57.1	7.10
62.3	8.72
67.4	11.40
α-*d*-Mannose	
45.3	0.208
47.3	0.227
52.8	0.272
54.2	0.308
61.6	0.409
64.2	0.447
68.7	0.521

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
β-*d*-Mannose	
47.9	0.204
52.3	0.246
58.1	0.318
65.0	0.411
69.5	0.487
74.0	0.589
***d*-Mannonic-γ-lactone**	
35.2	0.0938
41.9	0.123
48.7	0.173
55.6	0.250
59.0	0.288
70.0	0.424
α-Methyl-*d*-mannoside	
38.0	0.102
41.4	0.114
55.0	0.200
60.9	0.258
71.7	0.402
83.8	0.613

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
***d*-Mannonic-δ-lactone**	
39.4	0.0638
43.4	0.0752
47.6	0.0907
53.7	0.125
57.7	0.153
67.1	0.226
***d*-Mannitol**	
43.1	0.0203
46.3	0.0250
55.0	0.0391
62.7	0.0574
71.5	0.0845
79.7	0.1115
90.3	0.1487

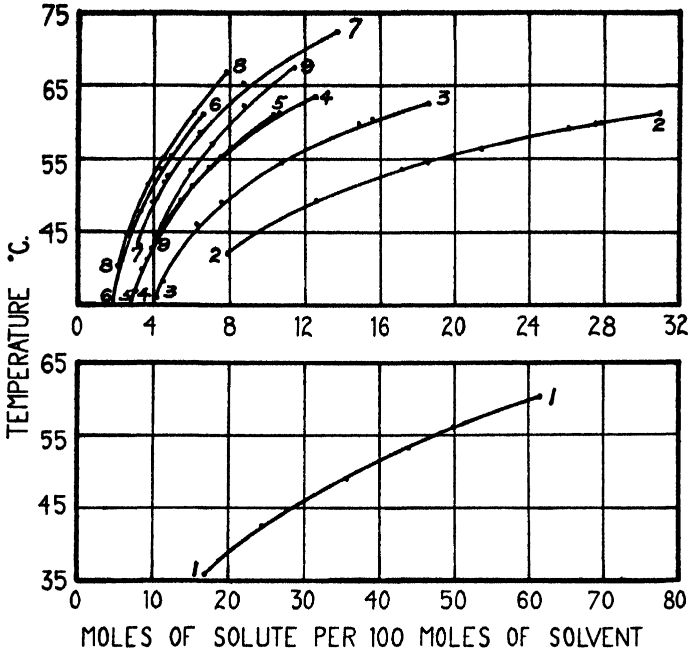

FIG. 2. SOLUBILITY OF *l*-RHAMNOSE IN ALCOHOLS

Curve 1, methyl alcohol; curve 2, ethyl alcohol; curve 3, allyl alcohol; curve 4, *n*-propyl alcohol; curve 5, isopropyl alcohol; curve 6, *n*-butyl alcohol; curve 7, *sec.*-butyl alcohol; curve 8, isobutyl alcohol; curve 9, *tert.*-butyl alcohol.

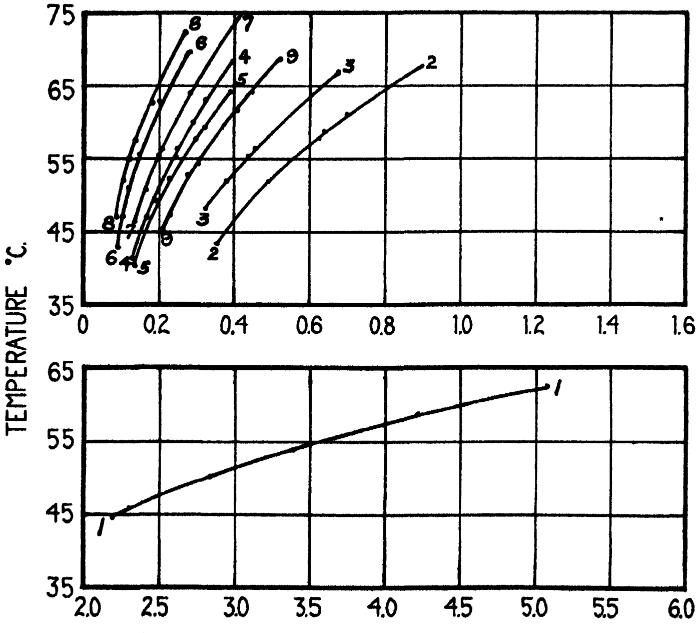

FIG. 3. SOLUBILITY OF α-*d*-MANNOSE IN ALCOHOLS (SEE FIGURE 2)

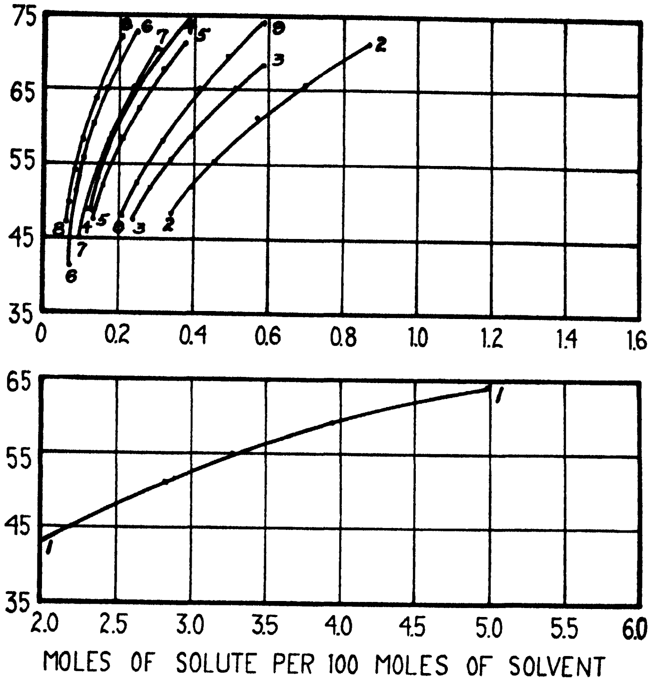

Fig. 4. Solubility of β-*d*-Mannose in Alcohols (See Figure 2)

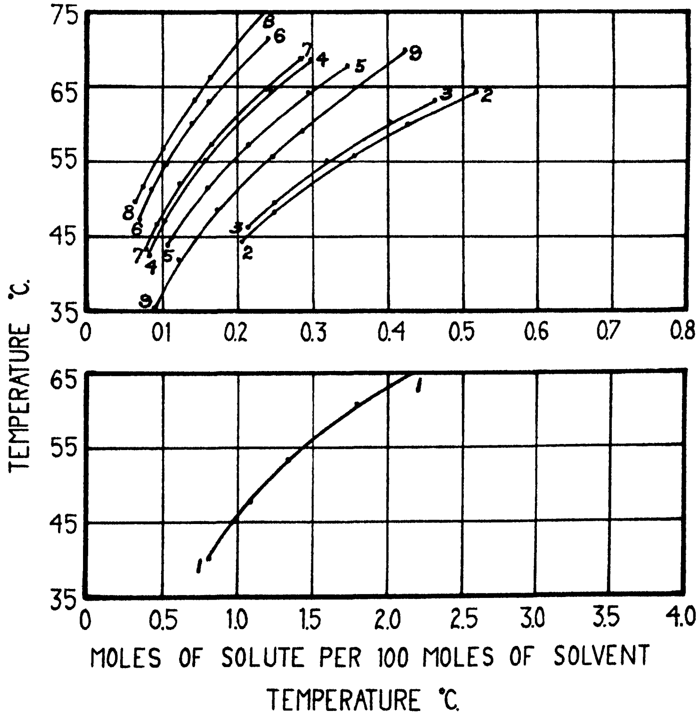

Fig. 5. Solubility of *d*-Mannonic-γ-lactone in Alcohols (See Figure 2)

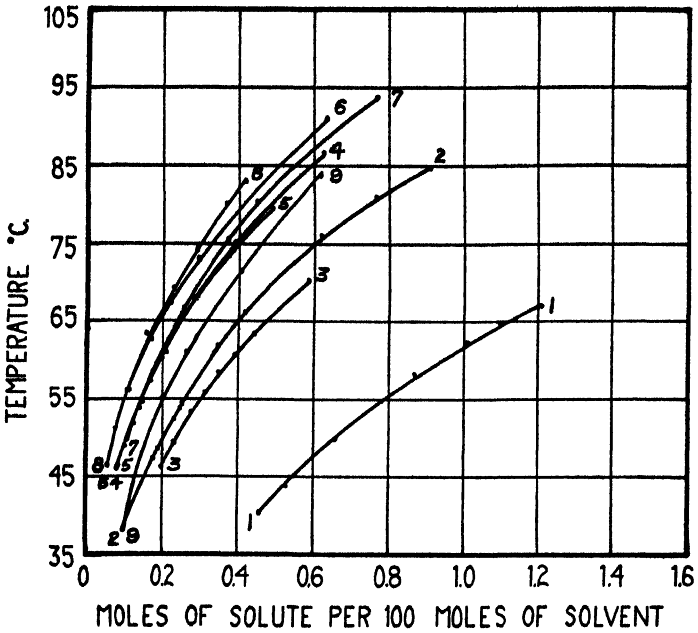

FIG. 6. SOLUBILITY OF α-METHYL-d-MANNOSIDE IN ALCOHOLS (SEE FIGURE 2)

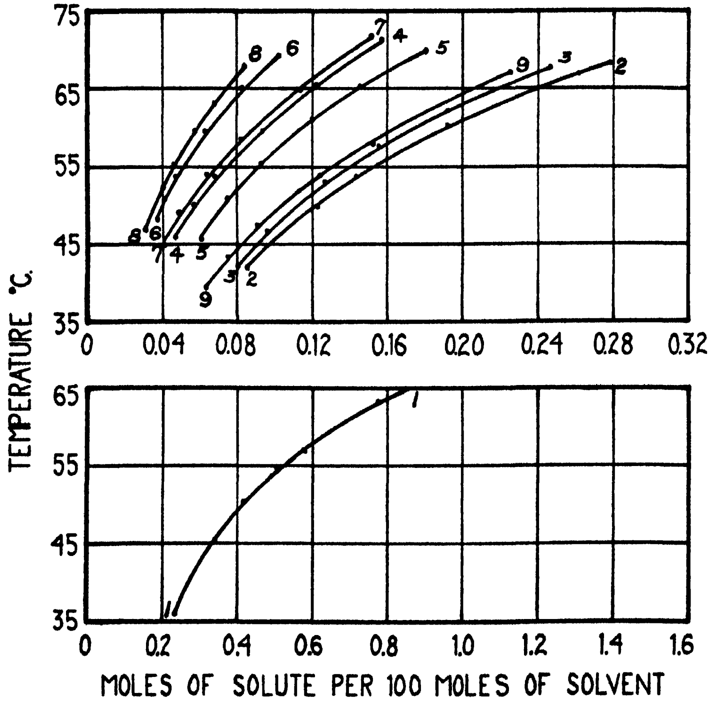

FIG. 7. SOLUBILITY OF d-MANNONIC-δ-LACTONE IN ALCOHOLS (SEE FIGURE 2)

crystal forms having different solubilities. The temperatures reported are for the type having the lower solution temperature.

Determinations made at temperatures higher than 90°C. are less reliable, owing to difficulty in controlling the temperature and in keeping the oil bath clear. No corrections were made for the alcohol in the vapor phase.

Solution temperatures for the seven sugar derivatives in the nine different alcohols are recorded in tables 2 to 10. The temperature is in degrees Centigrade and the concentration is expressed in moles per one hundred moles of solvent. The data are expressed graphically in figures 2 to 8.

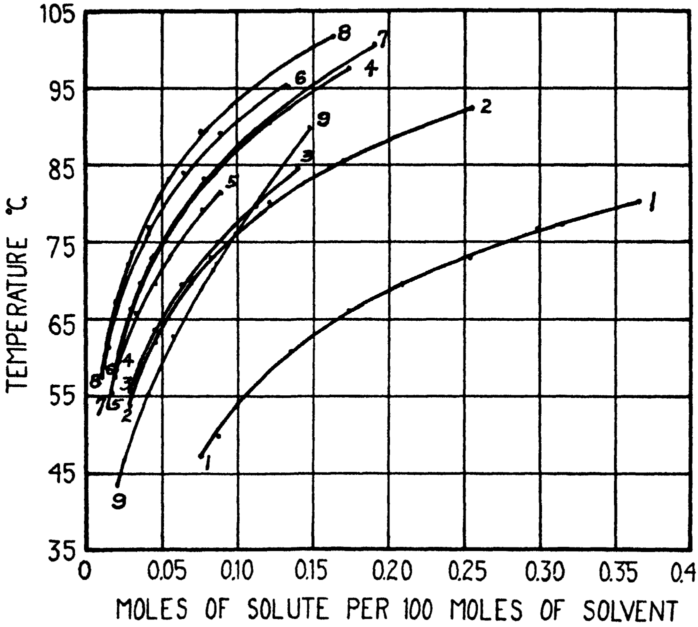

FIG. 8. SOLUBILITY OF *d*-MANNITOL IN ALCOHOLS (SEE FIGURE 2)

DISCUSSION OF RESULTS

In this study it has been possible to obtain information regarding the solubilities of a series of seven closely related isomeric compounds, of which six are of the *d*-rotatory variety and one of the *l*-rotatory variety.

In every solvent *l*-rhamnose, which was used in the form of its monohydrate, is many times as soluble as the next most soluble substance studied. α-*d*-Mannose is more soluble in all the alcohols than β-*d*-mannose, in the ratio of approximately 1.4 to 1. This is of special interest, since these isomeric forms of mannose differ only as regards the groups on the first asymmetric carbon atom. In most solvents α-methyl-*d*-mannoside is only slightly less soluble than β-*d*-mannose, but is considerably less soluble than α-*d*-mannose from which it is derived. The difference in solubility of *d*-mannonic-γ-lactone and *d*-mannonic-δ-lactone is pronounced.

The former is the more soluble in the ratio of approximately 2 to 1 in most alcohols, but over 3 to 1 in methyl alcohol. The relatively unstable δ-lactone thus has the lower solubility. The γ-lactone is more soluble than *β-d*-mannose in all the solvents. Of all the compounds studied, the polyhydric alcohol *d*-mannitol has the lowest solubility in all the alcohols.

The results of these studies confirm the general rules of solubility. All the solutes are polar compounds and hence their solubility in general decreases with increasing length of the carbon chain in the alcohols studied. All seven sugars are much more soluble in methyl alcohol (curve 1) than in any of the other alcohols. Second in solvent properties stands ethyl alcohol (curve 2), and allyl alcohol (curve 3) stands third. There is one exception; α-methylmannoside is somewhat more soluble in allyl alcohol than in ethyl alcohol. With the exception of rhamnose and of mannitol above 75°C., *tertiary*-butyl alcohol (curve 9) comes next in the series after allyl alcohol in the order of decreasing solvent action. We should expect it to be a better solvent than the other butyl alcohols, but not a better solvent than the propyl alcohols. With two exceptions, isopropyl alcohol (curve 5) is a slightly better solvent than normal propyl alcohol (curve 4). In the case of rhamnose and methylmannoside, the two alcohols have almost identical solvent properties. For all the sugars the remaining three butyl alcohols stand in the order secondary (curve 7), normal (curve 6), and isobutyl (curve 8). Thus there is agreement in the case of the propyl and butyl alcohols in that the secondary is a better solvent than the normal alcohol.

SUMMARY

1. Solubility data were determined by the synthetic method for seven carbohydrate derivatives in nine alcohols.

2. The concentration in terms of moles of solute per hundred moles of solvent and the solution temperature are given for each determination. The data are also presented graphically.

3. A comparison of the solubilities of the different solutes in the nine alcohols has been made.

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THE THERMAL DECOMPOSITION OF NITROMETHANE[1]

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In attempts during recent years to isolate data for unimolecular reactions the decomposition of various organic halides, ethers, azo compounds, amines, and nitrites has been studied kinetically, and though superficial results would suggest that in most cases a net reaction of the first order was occurring, extremely few are so free from secondary changes that the results may be accepted unequivocally. The multiplication of such attempts is thus justified. No nitro compounds have so far been studied. The simplest, nitromethane, was therefore chosen.

The apparatus and method used for the study were identical with those used previously by Taylor (3) in similar work, and involved the determination of the rate of pressure change of the reactant with time. To prevent condensation of the nitromethane vapor the apparatus outside the furnace was maintained at about 80°C. throughout the work. The nitromethane used was carefully fractionated from a Kahlbaum sample, the fraction boiling between 100.5 and 101°C. being collected. Temperatures from 390 to 420°C. were found to yield a convenient velocity of decomposition. The percentage increase in pressure during reaction was found to be 130, independent of temperature and pressure, as is shown in table 1.

Data of a typical experiment are given in table 2 showing the observed pressure increases occurring at the specified times at 420°C. with an initial pressure of 198 mm. of nitromethane.

The complete data are presented in table 3 in the form of fractional lives calculated as the times necessary for 25, 50, and 75 per cent of the total pressure increase to occur. This procedure is justified, since from the constancy of the end points under all conditions studied the same reaction is proceeding in each case.

From the general constancy of the above values, particularly for the quarter-lives at the higher temperatures, the reaction may be taken as of the first order, at least early in the reaction. The changing values of the three-quarter-lives would suggest the presence of secondary reactions of higher order than the first. In view of this possibility, the observed increase in the quarter-lives with decrease in initial pressure especially at the lower temperatures may be due either to a real deviation of the reaction from unimolecularity or to these secondary reactions of higher order which, if they should have lower temperature coefficients than the unimolecular

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[1] **Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1934.**

TABLE 1

Increase in pressure during decomposition of nitromethane

INITIAL PRESSURE	PER CENT INCREASE	INITIAL PRESSURE	PER CENT INCREASE
Temperature = 390°C.			
201	129	55.5	131
148	130	25.5	133
100.5	130		
Temperature = 400°C.			
201.5	130	52	133
156.1	130	26.5	130
101.5	131		
Temperature = 410°C.			
187.5	130	55	130
145	131	26.5	131
105.5	130		
Temperature = 420°C.			
198	130	51	130
157	130	27	129
104	131		

TABLE 2

Data of a typical experiment

Temperature, 420°C.; initial pressure, 198 mm.

TIME	PRESSURE INCREASE	TIME	PRESSURE INCREASE
minutes	*mm.*	*minutes*	*mm.*
1	40	25	234.5
2	67	30	240
3	89	35	243.5
4	108	40	246
5	124	45	247
6	138	75	249.5
8	161	334	251.5
10	179	469	253.5
15	208	1354	257
20	224.5		

reaction, would have a relatively larger effect on the overall rate at lower temperatures and higher pressures.

TABLE 3

Complete data for the decomposition expressed as fractional lives

INITIAL PRESSURE	FRACTIONAL LIVES		
	t_{25}	t_{50}	t_{75}
	Temperature = 420°C.		
mm.	*minutes*	*minutes*	*minutes*
198	1.40	4 00	7.50
157	1.40	4 00	7.00
104	1.50	4 00	7 50
51	1.40	3 50	7 50
27	1 38	4 00	7 50
	Temperature = 410°C.		
189	2 50	7 40	15.4
153	2 60	7 40	15.2
97.5	2 60	7 80	15.4
46.5	2 70	7 60	15 6
23.5	2 60	7 40	15.4
	Temperature = 400°C.		
201 5	5.10	14 0	28 0
156	5 12	14 0	28 0
101.5	5 50	14 0	28 0
52	5 20	13 0	25.0
26.5	5 30	14 0	24.0
	Temperature = 390°C.		
307	6 50		
202.5	8 00	21 0	42 0
148	10 40	27 0	51.6
100.5	10 35	27 5	52 1
55	10 40	29 0	61.0
25.5	10.40	32.0	63.0
	Temperature = 380°C.		
199.5	16.0		
146	16.5		
101	17.5		
49.5	21.0		
24.5	22.5		

To find the effect of increased surface the reaction vessel was filled with short lengths of Pyrex tubing, the ratio of surface to volume being increased 6.3 times. A comparison between experiments on the normal and increased surface is afforded by a typical run as shown in table 4. Taking the total pressure increase as 130 per cent for the reaction in the packed vessel as in the empty vessel, the quarter- and half-lives for the above reactions are 1.40 and 4.00 minutes in the empty vessel and 1.45 and 4.10 minutes in the packed vessel. The reaction in its early stages does not therefore appear to be influenced to any marked extent by surface.

TABLE 4

Comparison between experiments on the normal and increased surface

Temperature, 420°C.

TIME	INITIAL PRESSURE	
	Empty, 198 mm	Packed, 216 5 mm.
	Pressure increase	
minutes	*mm.*	*mm.*
1	40	50
2	67	87.5
3	89	115
4	108	136
5	124	152
6	138	162
8	161	181
10	179	190
20	224 5	205
40	246	206
50	247	202
60	248 5	199
80	249.5	193
170	250	188
260	251	192
1350	257	199

That the later reactions, however, are changed by the extent of surface can readily be seen from the peculiar pressure changes in the packed vessel given above, wherein the pressure increase reaches a maximum, falls, and then later rises again. This pressure decrease always observed in the packed vessel, though never found with the empty vessel, can be traced, as is shown later, to a condensation in the capillaries of some of the products of reaction. This fact is responsible for the apparent changed end point in the packed vessel.

The influence of foreign gases in the course of reaction was very thoroughly investigated for the following gases,—helium, nitrogen, nitric oxide, carbon dioxide, and oxygen. With the exception of oxygen all these gases were found to be without effect, the observed results, indeed, duplicating those already given. The addition of oxygen resulted in an appreciable change of the reaction rate and a somewhat different end point. The data are presented in table 5.

The energy of activation of the reaction in its early stages was found by application of the Arrhenius equation to the average values of the quarter-lives at the higher pressures as previously given. The logarithms of these times plotted against the reciprocals of the absolute temperatures gave a good straight line with a slope corresponding to 61,000 calories.

The actual mechanism of the reaction seems to be so extremely complex that it will be simplest to outline it step by step and to attempt to justify each step as given. The primary step postulated involves a split of oxygen according to the equation

$$CH_3NO_2 \rightarrow CH_3NO + \tfrac{1}{2}O_2$$

TABLE 5

The influence of oxygen on the reaction rate

Temperature, 420°C.; initial pressure of nitromethane, 102.5 mm.; initial pressure of oxygen, 79.5 mm.

TIME	PRESSURE INCREASE	TIME	PRESSURE INCREASE
minutes	*mm*	*minutes*	*mm.*
1	29.5	12	118.5
2	49.5	15	122.5
3	65	20	125.5
4	77.5	40	126
5	87.5	70	126
6	99.5	250	129
8	106	1350	130
10	113.5		

That nitrosomethane is formed fairly readily was demonstrated by refluxing nitromethane at its boiling point for forty-eight hours. The liquid was then fractionated and a small fraction boiling at 84°C. collected. This is the boiling point of formaldoxine, the isomer of nitrosomethane. Upon refluxing a small portion of this liquid with water for some hours and subsequent addition of silver nitrate a copious precipitate of silver cyanide was obtained, according to the reaction

$$CH_2{:}NOH \rightarrow HCN + H_2O$$

Another portion of the formaldoxime was hydrolyzed in presence of acid and gave a subsequent test for aldehyde

$$CH_2{:}NOH + H_2O \rightarrow CH_2O + NH_2OH$$

The proven presence of formaldoxime is indirect substantiation for the postulated nitrosomethane which is known to be unstable and to isomerize as stated (2).

Nitromethane is known to oxidize according to the reaction (1),

$$CH_3NO_2 + \tfrac{3}{4}O_2 \rightarrow CO_2 + \tfrac{3}{2}H_2O + \tfrac{1}{2}N_2$$

and gas analyses of the products of reaction showed their presence in large quantities. The reaction indeed must be a rapid one, as is demonstrated by the increased rate observed in the experiments with added oxygen as compared with those in its absence.

The third step involves the fate of the nitrosomethane; the simplest assumption would be the splitting into nitric oxide and free methyl radicals, which would give ethane alone or a mixture of methane, ethylene, and hydrogen, as frequently appears in hydrocarbon decompositions. Assuming the former,

$$2CH_3NO \rightarrow C_2H_6 + 2NO$$

there would be for the overall reaction occurring

$$10CH_3NO_2 \rightarrow 6NO + 6H_2O + 4CO_2 + 3C_2H_6 + 2N_2$$

The presence of large amounts of nitric oxide continually made itself felt during the conduct of the experiments. Copious brown fumes of the dioxide were always observed upon evacuating the system after each run.

In an effort to identify the above products and their relative amounts at the end of the decomposition a number of bombs were made up containing nitromethane; they were then heated to allow complete reaction to occur. The bombs upon cooling always showed large amounts of water. In some, definite tests for cyanides were obtained and others contained a white solid. A microanalysis of the solid[2] gave it the empirical formula CH_5NO_3, and it later proved to be ammonium bicarbonate. Analysis of the gases remaining in the bomb gave on the average 23 per cent carbon dioxide, 30 per cent carbon monoxide, 16 per cent methane, 4 per cent nitric oxide, about 1 per cent each of hydrogen and an unsaturated hydrocarbon reckoned as ethylene, with the residual 25 per cent of nitrogen. These analyses, bearing only superficial resemblance to the amount of products postulated above, suggested the possibility that concentration and surface conditions existing in the bombs might have a marked effect on the later progress of reaction. It will be recalled that although no effect of increased surface was found early in the reaction, the later stages were greatly changed. An observation of significance too, was that instead of copious brown fumes being observed on evacuating the system after runs with the increased surface, vapors with a strong ammoniacal odor alone were found. Close inspection of the capillaries after a number of these runs showed traces of the white solid, ammonium bicarbonate. Apparently one of the later reactions in the series is capable of being catalyzed to yield varying products; it is suggested as most likely that the nitrosomethane decomposition is responsible, since it is this reaction which yields the observed nitric oxide in large amounts with the empty vessel. The condensation of ammonium bicarbonate in the capillaries accounts satisfactorily for the pressure decrease observed with the increased surface and the reduced end point as compared with runs in the empty vessel. As stated previously, nitrosomethane will isomerize to formaldoxime, which in the presence of water from the nitromethane oxidation will hydrolyze to yield hydroxylamine and formaldehyde. The latter would be decomposed at the temperature in question into carbon monoxide and hydrogen. The hydroxylamine would yield ammonia, and hence give rise to ammonium bicarbonate in the system. It seems quite reasonable then, that the specific surface effect may be in the isomerization of the nitrosomethane to formaldoxime and, in view of the large amounts of nitric oxide produced in the runs in the unpacked vessel, to assume the mechanism given above. The overall reaction would then correspond to a pressure increase of 110 per cent as compared with the observed 130 per cent. If the reactions of the free radicals from the nitrosomethane should not give ethane alone, and the 16 per cent of methane in the bomb experiments would seem to suggest this, the total pressure change would be greater than that given above and more nearly in agreement with the observed.

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[2] Thanks are due Dr. Joseph B. Niederl for this analysis.

In summary then, the main reaction being studied appears to be a homogeneous unimolecular split of nitromethane into nitrosomethane and oxygen, with an energy of activation of about 61,000 calories. The complexity of the subsequent reactions does not permit a further analysis of the observed kinetic data.

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THE THERMAL DECOMPOSITION OF TRIETHYLAMINE[1]

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The marked similarity that has appeared up to the present in the decompositions of primary and secondary amines (3, 4, 5, 6) is significant, suggesting an explanation in the presence of the replaceable hydrogen in the amine group. The removal of this in a tertiary amine might be expected to cause a considerable change, since now the bond broken must certainly be C — N and hence data on this bond alone would be definitely available. At the same time it appeared possible that a study of the mechanism of the decomposition, hitherto neglected, might shed further light on existing difficulties in the reactions of the other amines.

The method of study again adopted was the static one, as in all previous cases, supplemented by analyses at significant points during the reaction. The triethylamine, originally an Eastman product, was stored over sodium to remove alcohol and water and distilled three times, the portion boiling between 88.7 and 90.3°C. being collected each time. The high boiling point of the amine necessitated that the capillaries and stopcocks connecting the amine reservoir, reaction vessel, and manometer be heated to prevent condensation. Since most of the measurements were made at pressures below atmospheric, a temperature of 80°C. was maintained throughout the parts of the system outside the furnace, proving sufficient for the purpose. The rate of pressure increase with time was measured at pressures from about 20 to 400 mm. at temperatures of 450, 470, 485, and 500°C.

The percentage increase in pressure for the end point of the reaction was extremely difficult to obtain, owing presumably to very slow secondary reactions occurring. Thus a sample of amine left in the system for six days at 450°C. increased in pressure 2 mm. between the sixth and seventh day. A rather arbitrary time limit was thus set at forty-eight hours at 450°C., this being reduced at the other temperatures studied by an amount in accordance with the observed temperature coefficient. In this way the pressure increase was found to vary from 200 to 250 per cent for the initial pressure range 350 to 20 mm. These values, however, were uninfluenced by temperature, as table 1 will show.

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1933.

Data for the individual experiments are most conveniently given as the times necessary for the pressure to increase by 25, 50, 75, 100, and 175 per cent of its initial value. At the lowest temperatures the times corresponding to the latter were not measured at all pressures and are therefore not listed in table 2.

The above values, especially those for 25 and 50 per cent pressure increase, being constant above about 150 mm. at 450°C., about 120 mm. at 470°C., about 50 mm. at 485°C., and at all pressures studied at 500°C. suggest that the reaction is of the first order, passing towards the bimolecular range at pressures below the limits stated.

TABLE 1

Relation between temperature and pressure increase

TEMPERATURE	INITIAL PRESSURE	PER CENT PRESSURE INCREASE
°C.	*mm.*	
450	25	258
450	128	221
450	242	205
470	21	256
470	317	201
485	33	254
485	286	205
500	17	268
500	161	216
500	347	194

The usual test for homogeneity of the reaction was made. The reaction vessel was packed with short lengths of Pyrex tubing sufficient to increase the surface to volume ratio a little more than seven times. Examples are given in table 3 of reactions in this packed vessel at 450°C. where no difference from the normal rates is shown.

The effect of additions of foreign gases was determined for nitrogen, ammonia, and hydrogen. The data given in table 4 were obtained.

It will be observed that experiments were made at the highest and lowest temperatures studied in each case and also at various pressures to include the effect of the added gas on the reaction in the pressure range where it appeared to have deviated from its unimolecular course. The effect of nitrogen is negligibly small at all temperatures and pressures studied. The same also applies to ammonia. Hydrogen on the other hand has a

TABLE 2

Times required for pressure to increase by certain per cent of its initial value

INITIAL PRESSURE	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
Temperature = 500°C.					
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
15	0 25	0 56	0.91	1.30	2.9
50	0 28	0 62	0 97	1.45	3.9
69	0 25	0 57	0 96	1.40	4 0
122	0 26	0 57	0.95	1.43	4.9
138	0.28	0.63	1.04	1.55	5.35
161	0.27	0 55	0 90	1.37	4.8
185	0 27	0 58	0 97	1.48	5 4
245	0 26	0 60	0.99	1 50	5.7
285	0.27	0 61	1 01	1 57	6 6
322	0 26	0 60	1 01	1.60	7.0
347	0.26	0 59	1 04	1.60	7.8
Temperature = 485°C.					
33	0 80	1.60	2.50	3.70	4.9
36	0.74	1 53	2 39	3.40	5.0
48	0 65	1 31	2.08	3 05	4.4
50	0 55	1 22	1 95	2 95	4.1
59	0 52	1 14	1.85	2.65	7.7
92	0.50	1 12	1.90	2 85	8.7
154	0.50	1 17	1 95	2 98	10.0
197	0 50	1.11	1.94	2.96	10.0
224	0.48	1.09	1.87	2.93	9.9
258	0 50	1 16	1.97	3.10	11.9
286	0.50	1 17	2 06	3.19	12.8
358	0.53	1 20	2 12	3.32	14.5
377	0.48	1.17	2.04	3 21	14.4
Temperature = 470°C.					
21	1 59	3.21	5.01	7 07	
29	1.44	2.78	4.40	6 88	
62	1.31	2 81	4.73	7.11	
66	1 22	2 65	4.53	6.93	
108	1 10	2.80	4.71	7.20	
130	1.03	2 55	4.45	6.78	
162	1.02	2.49	4.40	6 82	
217	1.05	2 59	4.47	6.91	
242	0 99	2.45	4.42	6.87	
297	1.03	2.57	4.46	6.89	
317	1 03	2.54	4.40	6 89	
407	1.02	2.47	4.42	6.92	

TABLE 2—*Concluded*

INITIAL PRESSURE p	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
Temperature = 450°C.					
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
25	4.0	9.0	16.0	23.2	
34	3.8	8.9	16.0	24.3	
50	3.7	8.7	14.8	22.5	
80	3.6	8.6	14.9	22.8	
102	3.3	8.2	14.5	22.5	
128	3.0	7.8	13.8	21.5	
150	2.7	6.9	12.2	18.9	
199	2.6	6.7	12.3	19.7	
242	2.8	7.4	13.5	21.3	
297	2.7	7.4	13.4	21.2	
330	2.7	7.3	13.3	21.2	
369	2.7	7.3	13.3	21.1	

marked effect. There is evidence that it accelerates the reaction slightly in its early stages both at low and at high pressures; the low pressure rate, however, is not raised to its high pressure value. Later in the reaction, as will be seen from a comparison of the times for 175 per cent increase in pressure in the presence and absence of hydrogen, the rate of pressure increase is markedly reduced and to such an extent that the pressure–time curve reaches a sharp maximum and actually decreases again slightly on continued heating. Whether the effect in the earlier stages is a true effect due to fruitful collisions cannot be said, but certainly the effect later in the reaction must be due to a hydrogenation.

To obtain the energy of activation of the reaction the logarithms of the average values of the times for 25, 50, and 75 per cent pressure increase in the high pressure range were plotted against the reciprocal of the absolute temperature. Excellent straight lines were obtained, the slopes however increasing steadily so that the energies calculated from them were 52,080 calories for 25 per cent, 55,550 calories for 50 per cent, and 57,300 calories for 75 per cent pressure increase. In itself this is sufficient indication that the reaction is complex and that the energy of activation of the earliest reaction occurring is less than 52,000 calories and would most probably be of the order of 50,000 calories. This value is higher than that found for the primary amines, namely 44,000 calories, but is in fair agreement with the value of 49,000 calories found for diethylamine.

The first attempt to obtain some idea of the products of reaction was made by interrupting a static run when only partially completed, removing the furnace from around the reaction vessel, and replacing it with liquid air. Only fixed gases should then remain, namely methane, hydrogen, or nitrogen. Thus, 222 mm. of amine after 10 minutes at 500°C. gave enough permanent gas at liquid air temperature to yield a pressure of 17 mm. Again, 384 mm. of amine after 23 hours at 450°C. gave a residual gas pressure of 28.5 mm. Assuming the simple gas laws to hold approximately, these figures show that the fixed gases constituted 65 and 60 per cent respectively of the initial pressures. This would indicate that only slight amounts of ammonia and unsaturated hydrocarbons were produced during the reaction. To decide this definitely about 0.2 g. of amine was sealed under its own vapor pressure at room temperature in a glass bomb and

TABLE 3

Reaction in vessel packed with Pyrex tubing

Temperature, 450°C.

INITIAL PRESSURE	FRACTIONAL LIVES			
	t_{25}	t_{50}	t_{75}	t_{100}
mm.	*minutes*	*minutes*	*minutes*	*minutes*
346	2.8	7.2	13.3	21.7
190	2.9	7.4	13.1	20.8

TABLE 4

Effect of added foreign gases

INITIAL PRESSURE		TEMPERATURE	FRACTIONAL LIVES				
Amine	Added gas		t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
mm	*mm*	*°C*	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
126	100 N_2	500	0.25	0.61	0.91	1.42	4.2
80	102 N_2	500	0.30	0.64	1.02	1.50	4.4
240	155 N_2	450	2.7	6.8	12.6	21.4	
170	150 N_2	450	2.7	7.0	12.5	19.4	
146	101 N_2	450	2.7	7.2		19.6	
81	100 N_2	450	3.5	8.1	14.4	21.6	
110	124 NH_3	500	0.28	0.61	1.03	1.55	5.3
73	143 NH_3	500	0.28	0.61	1.00	1.55	5.0
214	183 NH_3	450	2.8	7.2	13.0	20.0	
24	179 NH_3	450	4.0	8.7	14.4	22.0	
214	159 H_2	500	0.25	0.56	0.95	1.50	6.8
154	151 H_2	500	0.24	0.55	0.94	1.45	5.9
96	99 H_2	500	0.27	0.57	0.97	1.47	6.2
51	153 H_2	500	0.24	0.60	0.97	1.53	7.0
51	100 H_2	500	0.27	0.57	0.95	1.43	4.8
257	102 H_2	450	2.5	6.6	11.6	18.6	
175	143 H_2	450	2.4	6.2	11.2	17.7	
25	153 H_2	450	3.6	9.4	20.7		

thoroughly decomposed at 500°C. The gas remaining was then analyzed,[2] showing on the average of several determinations 58 per cent methane, 20 per cent ethane, 3 per cent ammonia, 2 per cent unsaturated hydrocarbon (bromine absorption), no hydrogen, and the residue 17 per cent nitrogen. In all such bomb experiments, owing to the high concentration of the reactant, large amounts of a tarry deposit always form—an occurrence never observed in the individual static runs.

Samples of the triethylamine were heated at 400°C. for from one to three hours to test for intermediate products early in the reaction. In the liquid which remained after heating, the presence of some primary amine was demonstrated by the Rimini test and of a hydrazine in quantity by reduction of alkaline silver nitrate. Cyanides, by the ferrocyanide and thiocyanate tests, acetonitrile by hydrolysis with hydrochloric acid, and secondary amines by the Simon test were shown to be absent. Analysis of the gas formed under these conditions showed the presence of 8 per cent ammonia, 3 per cent unsaturated hydrocarbon, less than 1 per cent of hydrogen, and the residue on combustion gave a CO_2 to H_2O ratio of 3 to 4. This would indicate the residual gas to be either propane or a mixture of methane and butane. A further sample of this gas therefore was kept in solid carbon dioxide until no further contraction in volume occurred. The uncondensed gas gave a CO_2 to H_2O ratio of 1:2.06. The condensed gas on vaporizing and combustion gave a ratio of 4:5.2. The residual hydrocarbon is then a mixture of methane and butane, the percentages of the total gas being 22 for methane and 35 for butane, leaving a residual 32 per cent of nitrogen.

Analysis shows then that butane is present in considerable quantities in the early stages of reaction. To account for this at the same time as a hydrazine the following reaction would seem to be indicated.

$$2(C_2H_5)_3N \rightarrow (C_2H_5)_2N{-}N(C_2H_5)_2 + C_4H_{10}$$

This would probably be a second-order reaction and would be followed by the decomposition of the hydrazine and also of the butane. If it is assumed that nitrogen and butane are formed by the hydrazine, the butane in turn yielding finally methane and ethane with residual carbon as always found, two molecules of amine would yield seven molecules of gaseous products corresponding to the pressure increase of 250 per cent observed. The butane decomposition, known to be relatively slow at 500°C., would account for the slow approach to the end point. If the hydrazine decomposition is relatively fast, as appears probable from the absence of any noticeable induction period, which would be expected since the initial bimolecular reaction involves no volume change, then the overall reaction in the intermediate stage would correspond to two molecules of amine yielding three of butane and one of nitrogen, approximately a two for one split. Now by the analytical method of Guggenheim (1) we can judge approximately the end point towards which a reaction is heading at any stage in its course, from three readings equally separated in time. The larger the time intervals the more accurate is the result. Applying this in three cases it is found that, at 500°C. for the first two minutes of reaction, corresponding to a pressure increase of 100 per cent, the end point should be 164 per cent and for two runs at 485°C. the end point should be 150 per cent. The errors involved in this determination do not justify the acceptance of these figures as absolute, but one fact would appear certain, namely, that the reaction in its early stages is more nearly a two for one split than the three or four for one necessary to account for the observed pressure increases of between 200 and 250 per cent.

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[2] These analyses and the subsequent tests after partial decomposition were kindly made by W. Takacs of this laboratory.

The mechanism suggested would appear so far to be satisfactory. The decomposition of the hydrazine would most probably be unimolecular, as is known to be the case for butane. The pressure increases herein measured would thus be those of a unimolecular volume increase reaction succeeding a bimolecular reaction without volume change. The relative rates of these would control the apparent order of reaction, but at a certain lower pressure the bimolecular reaction must eventually take control and the apparent order pass to more nearly two. Extremely little is known of the postulated tetraethylhydrazine, so that further speculation must be avoided.

In view of the presence of free ammonia and unsaturated hydrocarbon and in relatively larger quantities in the earlier than later stages of reaction, it would seem that some immediate decomposition of the amine into ammonia and an unsaturated hydrocarbon was occurring. The actual amounts found, however, preclude this possibility as of real significance in the major mechanism. The simultaneous presence of ammonia and unsaturated would account for the traces of primary amine found in the analyses. The effect of added ammonia, slight if any, could only be to aid such a reaction. The effect of added hydrogen, which is the more marked in the later stages of the reaction and especially on the end point, is to be accounted for by its known hydrogenation of unsaturateds formed in the butane decomposition (2).

SUMMARY

The thermal decomposition of triethylamine has been investigated over a pressure range from 15 to 400 mm. at temperatures from 450 to 500°C. The reaction is homogeneous with an energy of activation in its early stages of the order of 50,000 calories. The mechanism suggested by analysis of

intermediate products involves the formation of tetraethylhydrazine and butane with subsequent decompositions yielding chiefly methane and nitrogen.

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THE CHLORINATION OF PROPANE. II

The Heterogeneous Reaction

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In a previous communication (6) the results of studies on the homogeneous reaction occurring between chlorine and propane were presented. The present paper deals with the results obtained in the presence of catalysts.

PROCEDURE

The same flow method was used in this research as in the previous work on the homogeneous reaction. The per cent of chlorine converted was calculated from the iodine and hydrochloric acid titrations in the potassium iodide absorbers. The reactants were purified, measured, and mixed before being passed into the heated contact mass.

At the beginning of a series of runs, a new catalyst was placed in the reaction chamber and activated with nitrogen at 400°C. for about two hours. This was followed with chlorine at about 200°C. for thirty minutes, and the excess chlorine was swept out with nitrogen at room temperature.

MATERIALS

The silica gel used as a catalyst base was obtained through the courtesy of the Silica Gel Corporation. It was a gel prepared by the method of Patrick and contained some iron. The gel was purified by boiling with concentrated nitric acid and then with distilled water until acid-free, dried on a steam bath, and activated with clean dry air at 270°C.

The catalysts were prepared by the method of Smith and Reyerson (5). A solution of $Cu(NH_3)_4(NO_3)_2$ or $Cu(NH_3)_4Cl_2$, depending upon the catalyst wanted, was made while the gel was activated at 350–400°C. The gel was allowed to cool and the copper solution poured over it. The impregnated gel, which was blue, was placed between filter papers to dry. The method from here on depended upon the type of catalyst wanted, namely, metallic copper, or cupric chloride on the gel.

If the copper gel was wanted the $Cu(NH_3)_4(NO_3)_2$ gel was placed in the furnace and dry air or oxygen passed over it. This was then reduced to metallic copper by passing a stream of hydrogen at 450°C. over it until reduction was complete. In the production of the cupric chloride catalyst, the gel impregnated with $Cu(NH_3)_2Cl_2$ was placed in the catalyst tube and activated as described previously.

TABLE 1

Chlorination of propane using Al_2O_3 *as catalyst*

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
98	535	473	21	494	4.3
135	516	428	57	485	11.8
151	503	380	100	480	20 8
166	475	315	172	487	35 3
179	427	207	279	486	57.3
187	413	175	338	513	65.9
191	454	54	425	479	88 7
199	415	4	619	623	99.2

TABLE 2

Chlorination of propane using Al_2O_3 *as catalyst*

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
62	632	368	2	320	0 6
97	662	304	5	309	1.6
139	637	272	31	303	10.2
148	635	288	41	329	12 5
160	643	263	73	336	21.8
171	625	233	109	342	31.8
182	619	187	130	317	41 0
187	601	161	176	337	52.1
193	600	122	213	335	63.5
201	600	75	280	355	78.9
205	564	50	301	351	85.6
208	588	50	304	354	86.0
208	574	54	304	358	84.8
211	575	10	365	375	97.4

The aluminum oxide catalyst was furnished through the kindness of the Aluminum Company of America. It was an excellent uniform product of 8–14 mesh that had been specially activated. Its catalytic behavior was tested in dehydration reactions in which olefins were pyrogenically made from the corresponding alcohol. The results showed the catalytic activity to be excellent.

This activated alumina was slightly reddish in color, which was probably due to the presence of traces of iron. After activating it for eight hours with nitrogen, the temperature rose from 20°C. to 40°C. when the reactants were passed through it, indicating good absorptive powers.

DISCUSSION OF RESULTS

The runs in this group were divided into two series, namely, determinations at 10 liters per hour for the total rate of flow and at 20 liters per hour. One series of runs was made at 2 liters per hour using a copperized gel catalyst. No further runs were made at this rate, as poisoning is high at such low space velocities. A few runs were made at 50 liters per hour, but the problem of heat transfer was so great that the results obtained were not valid.

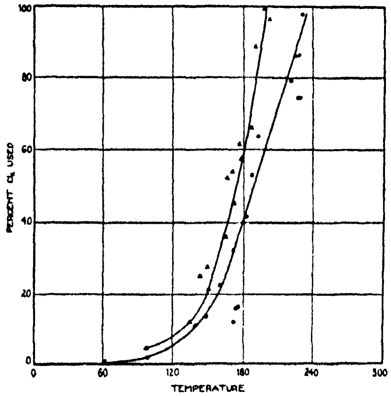

FIG. 1

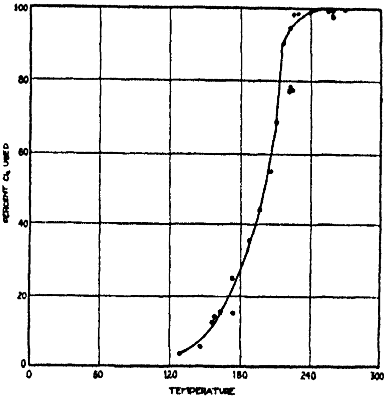

FIG. 2

FIG. 1. CHLORINATION OF PROPANE USING Al_2O_3 AS CATALYST AND A RATE OF FLOW OF TWO LITERS PER HOUR

⊙ $C_3H_8:Cl_2 = 2:1$; △ $C_3H_8:Cl_2 = 1:1$

FIG. 2. CHLORINATION OF PROPANE USING $CuCl_2 \cdot SiO_2$ CATALYST AND A RATE OF FLOW OF TEN LITERS PER HOUR

$C_3H_8:Cl_2 = 2:1$

A series of runs was made using an activated aluminum oxide catalyst, the results of which are summarized in figure 1 and tables 1 and 2. It was believed that a layer of aluminum chloride would form on the aluminum oxide base and thus give a very active catalyst. The $AlCl_3 \cdot Al_2O_3$ combination was desired, as aluminum chloride if used alone would sublime and leave the reaction chamber. It was hoped that the aluminum oxide would prevent this.

In comparing the data represented in figure 1 with similar data in the other catalytic runs it can be seen that the aluminum oxide catalyst was quite active. Nevertheless, it proved to be undesirable. Water was found to be continually coming over with the products of the reaction, and on examination the catalyst proved to be saturated with water. The probable reaction is as follows:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

This water undoubtedly reacted with chlorine to give hypochlorous acid. How this would affect the propane or the course of chlorination is unknown, but it would not simplify matters. The use of this catalyst was consequently discontinued, and only the $CuCl_2 \cdot SiO_2$ gel catalyst used. The latter catalyst was active and easy to prepare.

The question of the dehydrogenation of propane prior to chlorination arises in the catalytic reaction. Frey and Huppke (2) have recently studied the dehydrogenation of propane. They give the following equation for the affinity of the reaction:

TABLE 3

Chlorination of propane using $Cu–SiO_2$ *catalyst*

60 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
52	1030	1018	2	1020	0 2
103	1012	1184	12	1196	1 0
145	819	976	106	1082	9 8
153	1056	921	135	1056	12 8
164	955	786	224	1010	22 2
184	843	580	463	1043	44 3
204	726	411	742	1153	64.3
209	595	193	923	1116	82.7
225	632	34	994	1028	96 7
246	413	14	1132	1146	98 8
276	448		1397	1397	100.0

$$A = 25{,}920 - 9.21T \log_{10}T - 0.21T$$

Since all of the chlorinations were made below 300°C., we shall use this temperature for the calculation.

Then

$$A = 25{,}775 \text{ cals.}$$

$$A = -RT \ln \frac{(C_3H_6)(H_2)}{(C_3H_8)}$$

Substituting the proper values, we find the equilibrium partial pressure of propylene at 300°C. to be 1.3×10^{-5} atmospheres. This small concentration should scarcely affect the results at even the higher temperatures. The factor involving the addition of chlorine to propylene, formed by the pyrolysis of propane, may then be disregarded.

An examination of the graphs giving the results of the catalytic reaction shows the difficulty of obtaining uniform results. Only the runs having a high partial pressure of propane will give a uniform curve. This is due to two effects: first, the high chlorine partial pressure causes the production of relatively large amounts of the higher chlorinated propanes which act as poisons, and second, the occurrence of a new phenomenon which we have called catalytic hysteresis (to be mentioned later). If a poisoning of the wall in the empty chamber reaction had an appreciable effect on the reaction, certainly such a powerful adsorbent as silica gel, with its enormous surface, should greatly affect the rate of the reaction.

TABLE 4

Chlorination of propane using $CuCl_2 \cdot SiO_2$ *catalyst*

5 minutes duration. Total rate of flow 10 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
107	547	258		258	
146	533	242	14	256	5.5
222	485	15	256	271	94.3
158	542	227	37	264	14.0
173	591	210	68	278	24.5
187	529	175	96	271	35.4
205	492	118	141	259	54.4
221	500	63	207	270	76.7
226	470	5	287	292	98.2
156	541	242	34	276	12.3
173	532	217	37	254	14.6
196	514	139	108	247	43.7
222	498	57	203	260	78.0
163	538	231	41	272	15.1
210	498	80	172	252	68.2
229	468	4	291	295	98.5
240	465	4	284	288	98.5
216	480	27	246	273	90.0
240	465	5	303	308	98.2
256	452	4	287	291	98.5
270	450		301	301	100.0
224	477	61	195	256	76.2
260	452	8	258	266	96.8
260	448	1	293	294	99.8
223		115	147	262	56.0
129	565	270	10	280	3.6

In order to calculate the heat of activation, a series of runs is chosen having a high partial pressure of propane, as the results are fairly uniform under these conditions. Using the data in figure 2 (table 4), the ratio of the velocity constants k_2/k_1 is equal to 2 in the temperature range 168°C. to 192°C.

$$\ln\frac{k_2}{k_1} = \frac{H}{R}\,\frac{T_2 - T_1}{T_2T_1}$$

$$\begin{aligned} H &= \frac{RT_2T_1 \ln k_2/k_1}{T_2 - T_1} \\ &= \frac{2 \times 465 \times 441 \times \ln 2}{465 - 441} \\ &= 11{,}900 \text{ calories per mole } (\mathrm{CuCl_2 \cdot SiO_2} \text{ catalyst}) \end{aligned}$$

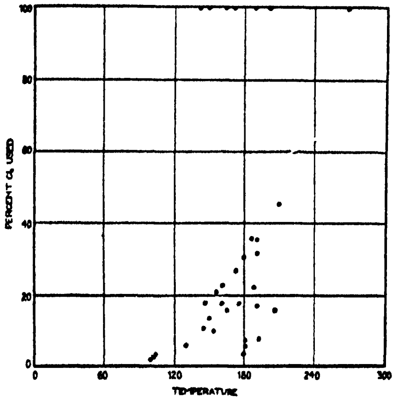

FIG. 3

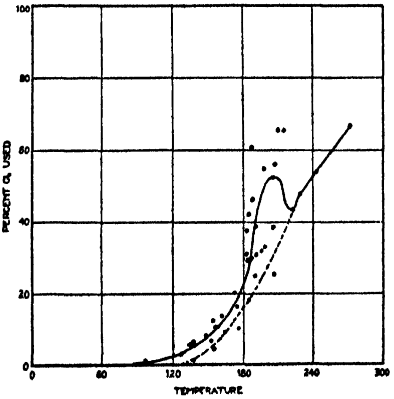

FIG. 4

FIG. 3. CHLORINATION OF PROPANE USING $\mathrm{CuCl_2{\cdot}SiO_2}$ CATALYST AND A RATE OF FLOW OF TEN LITERS PER HOUR

$\mathrm{C_3H_8{:}Cl_2} = 1{:}2$

FIG. 4. CHLORINATION OF PROPANE USING $\mathrm{CuCl_2{\cdot}SiO_2}$ CATALYST AND A RATE OF FLOW OF TWENTY LITERS PER HOUR

$\mathrm{C_3H_8{:}Cl_2} = 1{:}1$

The heat of activation is almost half of that calculated for the empty chamber results. Not only is the heat of activation less in the catalytic reaction, but an examination of corresponding data will show a greater extent of chlorination at a given temperature and a given rate of flow when the contact agent is present.

The heats of activation for the copperized gel catalyst and the aluminum oxide catalyst were calculated and found to be 14,400 and 12,900 calories per mole, respectively. The data from the copperized gel (see table 3) were taken when the partial pressures of the reactants were equal. In these catalytic reactions, very little change in rate was detected when the partial pressures of the reactants were varied.

Figure 4 gives a good example of the effect of poisoning on the catalyst. The continuous curve represents one series of successive runs. The negative temperature coefficient of reaction is shown here just as in the empty chamber runs. In order to prove that this effect was due to poisoning, the catalyst was used for some time and another series of runs was made. The results followed the broken line curve, which makes a normal uniform chlorination curve with the upper part of the original curve. After the contact agent had been completely poisoned or when it had reached a steady state of activity, no abnormalities were noticed.

MECHANISM OF THE CATALYTIC REACTION

Cupric chloride at higher temperatures dissociates (4) and gives off free chlorine. This chlorine is probably in the atomic form when first liberated.

$$CuCl_2 + \text{heat} \rightarrow CuCl + Cl$$

Such a contact mass should be a good agent for the production of chlorine atoms with this possible mechanism.

$$\begin{gathered} CuCl + Cl_2 \rightarrow CuCl_2 + Cl \\ CuCl_2 + \text{heat} \rightarrow CuCl + Cl, \text{ etc.} \end{gathered}$$

These chlorinations may initiate chains just as in the mechanism postulated for the gas phase chlorination.

$$\begin{gathered} C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl, \text{ etc.} \end{gathered}$$

It may be that the free propyl radicals also combine with chlorine atoms on the surface:

$$C_3H_7 + Cl \rightarrow C_3H_7Cl$$

Cuprous chloride has the property of combining with hydrogen chloride to give a complex.

$$CuCl + HCl \rightarrow HCuCl_2$$

This property of cuprous chloride should make it a good catalyst for chlorination, as it aids in the removal of the hydrogen chloride. We may represent the reaction at the surface as follows:

$$\begin{gathered} CuCl_2 + \text{heat} \rightarrow CuCl + Cl \\ CuCl + Cl + C_3H_8 \rightarrow HCuCl_2 + C_3H_7 \\ HCuCl_2 + \text{heat} \rightarrow CuCl + HCl \\ CuCl + Cl_2 \rightarrow CuCl_2 + Cl \\ Cl + C_3H_7 \rightarrow C_3H_7Cl \end{gathered}$$

Since some of the chlorination takes place in the gas phase, both the gas phase and surface mechanism would take place simultaneously. The quantitative extent of the two processes has not been determined.

CATALYTIC HYSTERESIS

A new and peculiar effect occurred in the catalytic runs using partial pressures of chlorine of 0.5 atmosphere or over. Starting a series of runs at a low temperature and going up the temperature scale gave a curve that was quite normal up to the point where all the chlorine had reacted. In dropping the temperature, the points did not fall along the curve obtained with a successively rising temperature. One hundred per cent of the chlorine continued to be used as the temperature in the reaction chamber was dropped to as low a point as 140°C. The series of points at 100 per cent on figure 3 illustrate this phenomenon. Figure 5 gives a typical hysteresis curve with the points numbered in the order in which the determinations were made.

The possibility of hysteresis at lower conversions than 100 per cent was tested, but in each case, on lowering the temperature, the points followed the original curve. It seemed necessary to carry the reaction to 100 per cent conversion before this reaction inertia set in.

A freshly activated catalyst produced this effect with greater ease than one that had been used for some time. In two cases, with extremely active catalysts, the catalytic hysteresis set in between 170°C. and 190°C. This was at a much lower temperature than usual.

An examination of the figure showing this effect indicates 100 per cent conversion where the normal conversion at the same temperature would be around 5 per cent. Equilibrium had been established at the lower temperatures, as runs made over a period of two or three hours gave constant results. The hysteresis effect remained as long as five hours after its inception, this period of time being certainly sufficient for the attainment of equilibrium. The temperature indicated by the thermometer was correct, as the thermometer well went to the center of the contact mass.

One of the possible explanations advanced for this phenomenon was briefly this: chlorination at a low temperature permits the adsorption of chloropropanes (not so strongly adsorbed at higher temperatures) which poison the catalyst. Higher temperatures favor the activation of the catalyst by removing the adsorbed products. This autoactivation enhances the activity of the contact mass, thereby producing a high percentage of chlorination.

To test this possible theory, nitrogen was passed over the catalyst at 300°C. to activate it thoroughly. The temperature was then dropped to 140°C. and the reactants passed through the reaction zone. If the theory was correct, 100 per cent chlorination should be the result, but such was not the case. A second explanation was advanced, which involved the origin of the heat of activation. This energy is derived from two sources: the heat of reaction and the heat of the electric furnace.

$$H_{\text{furnace}} + H_{\text{reaction}} = E_{\text{activation}} + H_{\text{losses}}$$

At the beginning of a series of runs the extent of reaction is such that $H_F + H_R$ is insufficient to activate all of the molecules. As soon as there is energy enough to activate all of the molecules, there will be 100 per cent conversion. Once this condition is attained, $H_F + H_R$ is more than enough to activate all of the molecules, and even though H_F is decreased (the temperature dropped), all of the molecules will still be activated. A point will be reached when the two sides of the equation will be exactly equal. Any decrease in temperature beyond this point will decrease the heat resulting from reaction (H_R) as well as H_F, which in turn means that the energy available for activation is cut. These two factors H_R and E_A will affect one another progressively, and there should be a sudden drop in the extent of chlorination.

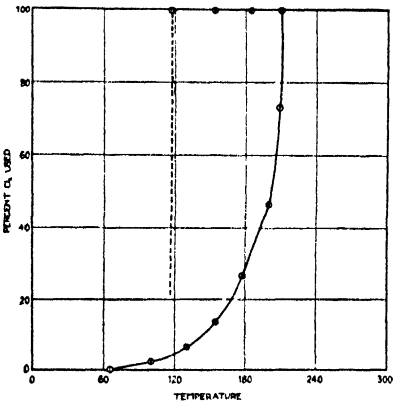

FIG. 5

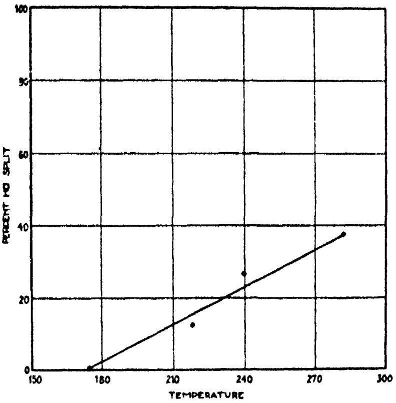

FIG. 6

FIG. 5. A TYPICAL HYSTERESIS CURVE

FIG. 6. RELATIONSHIP BETWEEN AMOUNT OF HYDROGEN CHLORIDE SPLIT AND THE TEMPERATURE

The question arises as to why this effect does not take place in the homogeneous reaction. In all probability it does, but to such a small extent, because of the small surface involved, that it has not been detected. In addition, the heat of activation of the catalytic reaction is almost half of that of the gas phase reaction.

PYROLYSIS OF PROPYL CHLORIDES

Hurd (3) gives many examples of the pyrolysis of the alkyl halides. No mention of the propyl chlorides is made, but Aronstein (1) studied the effect of heat on *n*-propyl bromide. At 280°C. this compound rearranged into the iso-form. Such a behavior might involve the splitting out of hydrogen bromide. A similar behavior would be expected in the case of propyl chlorides.

The catalytic hysteresis offered an excellent means of studying this pyrolysis. It had been postulated that secondary chlorination of paraffins having two or more carbon atoms could take place in two ways. The first method was by direct substitution.

$$RCH_2CH_2Cl + Cl_2 \rightarrow RCHCl \cdot CH_2Cl + HCl$$

and the second by pyrolysis followed by addition:

$$\begin{array}{l} RCHCl \cdot CH_3 \\ \quad\text{or} \\ RCH_2 \cdot CH_2Cl \end{array} + \text{heat} \rightarrow RCH{=}CH_2 + HCl$$

$$R \cdot CH{=}CH_2 + Cl_2 \rightarrow RCHCl \cdot CH_2Cl$$

Both of these mechanisms give the same final products, and there would be no way of determining the ratio of the two processes. The equation for the first mechanism gives the more symmetrical chloropropane, but it would have been possible to attach the second chlorine atom to the terminal carbon. In such a case the product obtained by the two mechanisms would not have been the same. The analysis of products of chlorination showing relatively high quantities of the 1,2-dichloro compounds might indicate the pyrolytic mechanism of secondary chlorination but would not definitely prove it.

In a normal chlorination, one molecule of hydrogen chloride is formed for each chlorine molecule used, regardless of the mechanism of chlorination. This supposition is the basis of the calculations for obtaining the per cent of chlorine used in this research. The unused chlorine and the hydrogen chloride formed during chlorination were passed through a solution of potassium iodide. After removing this solution from the absorption chambers it was progressively titrated with standard thiosulfate and potassium hydroxide.

$$(\text{cc. } Na_2S_2O_3) \times \text{normality factor} \times 11.2 = \text{cc. } Cl_2 \text{ unused}$$
$$(\text{cc. KOH}) \times \text{normality factor} \times 22.4 = \text{cc. } Cl_2 \text{ used}$$

The sum of these two quantities will give the total chlorine admitted into the system. This should agree with the setting of the chlorine flowmeter, if the reaction is behaving in a normal manner.

Once the reaction reaches the stage where all the chlorine is used, the effect of the hydrogen chloride split will be noticed, as there is no excess chlorine to satisfy the unsaturation of the substituted and unsubstituted propylenes. At this point, the calculated chlorine input (from chemical data) will be higher than that indicated by the flowmeter.

$$RCH_2 \cdot CH_2Cl + \text{heat} \rightarrow RCH{=}CH_2 + HCl$$

When such a process takes place and the unsaturated compound formed is not saturated by the addition of chlorine, two molecules of hydrogen chloride will be formed for each chlorine molecule used. The product collected should have unsaturated compounds present. The difference between the calculated chlorine input and that indicated by the flowmeter should give a measure of the hydrogen chloride split.

The hysteresis effect enables us to go to lower temperatures while still retaining 100 per cent chlorine used, which in turn allows a study of the relationship between the amount of hydrogen chloride split and the temperature. A regular decrease in pyrolysis would be expected with a decrease in temperature. This was actually the case, as is illustrated by figure 6 (see table 5).

TABLE 5

Chlorination of propane using $CuCl_2 \cdot SiO_2$ *catalyst*

5 minutes duration. Total rate of flow 10 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
240	256	1	527	528	99 9
218	212		469	469	100 0
174	195		418	418	100 0
282	250		572	572	100 0

Since this elimination of hydrogen chloride takes place when the chlorine used is not 100 per cent, we have a rough way of estimating the extent of chlorination due to the addition of chlorine to the unsaturated compounds. For instance, at 200°C. the per cent of hydrogen chloride split out of the chlorinated propanes would be roughly the same if there was an excess of chlorine gas or if the hysteresis was present. It would be expected then that the amount of 1,2-dichloropropane formed when an excess of chlorine was present would be measured by the extent of the hydrogen chloride split under hysteresis. This is, of course, supposing that every molecule which has had hydrogen chloride removed, remains as such and does not add either hydrogen chloride or chlorine at the double bond. The figure shows that secondary chlorination by the pyrolytic mechanism is quite appreciable at the higher temperatures. It might well be that most of the secondary chlorination takes place by this process.

Cuprous chloride can combine with hydrogen chloride to form a complex:

$$CuCl + HCl \rightarrow HCuCl_2$$

This should favor its catalytic property for the removal of hydrogen chloride from a compound.

COUPLING REACTION

Evidence of coupling reactions has been obtained by the analysis of products from chlorinations. Any discrepancy between the calculated and flowmeter input when an excess of chlorine was present should indicate a coupling reaction.

$$RCH_2Cl + CH_3R \rightarrow RCH_2 \cdot CH_2R + HCl$$

In this way some of the chlorine molecules would give two molecules of hydrogen chloride instead of one as in a normal chlorination. A few runs were made which brought out this coupling reaction. In all the cases there was an excess of chlorine in the exit gases, but the calculated chlorine input exceeds the value indicated by the flowmeter. The catalyst was always poisoned by use, reducing its ability to remove hydrogen chloride from the propyl chlorides. The temperature of reaction was high (324°C.). The formation of free radicals would be favored by such a condition and the possibility of coupling taking place was increased.

PRODUCT

The product obtained from the catalytic runs was more highly chlorinated than the chloropropanes resulting from the gas phase reaction. A high partial pressure of propane favored the production of the lower chloro derivatives. 1,2-Dichloropropane was found in relatively large amounts in all of the samples collected. This would indicate that a large amount of the secondary chlorination takes place by the addition of chlorine to propylene formed by the pyrolysis of monopropyl chloride. The product collected at low temperatures during hysteresis showed a lower chlorine content than the higher temperature runs under the same conditions. Under the conditions studied, no orientation tendency was shown by the catalysts towards the chlorination.

In all cases in which there was 100 per cent chlorine used, the product had a peculiar pungent odor that was not characteristic of saturated chlorohydrocarbons. Along with this peculiarity in odor, etc., it was found that the composite samples were unsaturated, as was shown by their bromine adsorption.

SUMMARY

1. The catalytic reaction of propane with chlorine has been studied under various conditions.

2. A mechanism for the reaction has been postulated.
3. Heats of activation were calculated for the three catalysts used.
4. High partial pressures of chlorine tend to poison the catalyst.
5. A "hysteresis effect" was found and an explanation postulated.
6. Secondary chlorination in part was shown to be due to the addition of chlorine to propylene formed by the pyrolysis of propyl chlorides.
7. A coupling reaction was shown to be present.
8. High chlorine partial pressures, high temperatures, and high rates of flow all favored the formation of more highly chlorinated products.
9. A relatively large per cent of 1,2-dichloropropane in the products supported the statement made in 6.
10. Unsaturation was found in all products collected when the chlorine used was 100 per cent.

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THE ALUMINUM ALKYL OXIDES AND THEIR PARACHORS

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Sugden (9), in deriving the atomic parachor of aluminum from measurements on the acetylacetonate, propionylacetonate, and bromide, found it necessary to formulate these compounds with singlet linkages (i.e., one-electron valency bonds) in order to obtain reasonable values for the parachor of aluminum, each singlet linkage decreasing the observed parachor by 11.6 units. No measurements have been made on simple compounds of aluminum. In the case of thallium the singlet linkage formulation of analogous compounds has been supported by measurements on the ethoxide, nitrate, formate, and acetate, because both types gave the same value for the parachor of thallium, provided that the chelated compounds were assigned a singlet linkage formulation. The force of this argument was, however, diminished by the demonstration (7) that thallium ethoxide is a fourfold polymer, while the chelated ethyl acetoacetate is bimolecular. Since the parachor of aluminum has not been obtained from simple unchelated compounds, work was commenced on the alkyl oxides of aluminum, a group of liquids and low-melting solids, but it was found that these compounds are by no means simple in structure. Nevertheless, a number of points of interest have been noted which are worthy of record.

EXPERIMENTAL

Alumino acetylacetonate, prepared by Sugden's method (9) for the propionylacetonate, melted at 192°C. after recrystallization from alcohol and benzene. Density determinations were made in a U-shaped pyknometer (8), and surface tensions were estimated by the double capillary method. The method was checked frequently by determinations on standard liquids.

T	γ	D	P
°C.			
195	20.17	1.007	686.5
210	18.74	0.989	686.8
220	17.92	0.976	683.6

Mean P = 682.9, whence P_{Al} = 43.9

Alumino ethyl acetoacetate was prepared by adding the ester to aluminum under petroleum ether, the aluminum being activated by the method of Wislicenus and Kaufman (12). Reaction proceeded for an hour without warming, yielding a pale green viscous oil, b.p. 190–200°C. at 11 mm., which solidified in the presence of petroleum ether; after recrystallization from this solvent the substance melted at 78–79°C.

T	γ	D	P
°C.			
80	27.20	1.101	859.0
95	25.80	1 088	857.6
110	24.32	1.074	857.0
125	23.00	1.059	856.5
140	21.60	1.042	857.0

Mean P = 857.4, whence P_{Al} = 41.4

Alumino diethyl malonate was prepared by the prolonged heating of aluminum and mercuric chloride with malonic ester. The petroleum ether extract deposited white crystals melting at 95–96°C. after several recrystallizations from petroleum ether.

T	γ	D	P
°C.			
100	24.02	1.084	1030
120	22 13	1.064	1029
140	20.62	1.047	1027

Mean P = 1029, whence P_{Al} = 36.0

Chromium acetylacetonate. Equivalent quantities of chromium sulfate and acetylacetone were mixed in aqueous solution, and the chromium was precipitated by ammonium hydroxide. After forty-eight hours the acetylacetonate crystallized in red needles which were extracted with benzene; the benzene layer was dried and evaporated. The acetylacetonate was then purified by sublimation *in vacuo*; it melted at 212°C.

T	γ	D	P
°C.			
213	21.24	1.072	699 5
225	20.20	1.059	699.2
240	18.92	1.042	698.8

Mean P = 699.2, whence P_{Cr} = 60.2

Aluminum alkyl oxides were prepared by the method of Tistschenko (11) and purified by distillation under reduced pressure. As the whole preparation always distilled over approximately a five-degree range with very small head and tail fractions, no special precautions were taken for fractionation, the material being evidently homogeneous. Parachor determinations were made on a redistilled middle fraction. Obtained in this way the oxides were viscous liquids or white non-crystalline solids with ill-defined melting points, often exhibiting marked supercooling, the extreme case being the isopropoxide, m.p. 118°C., which has been supercooled to −20°C. without solidification. Analyses were made by dissolving the oxides in acid, and precipitating and weighing the alumina in the usual manner. Analysis was also attempted by evaporation of the oxide with water and ignition of the resulting alumina, but this method invariably gave high results, e.g., the butoxide gave 11.60 and 11.29 per cent Al (calculated, 10.95 per cent). The same peculiarity is to be found in the analyses of Gladstone and Tribe (3), although no reference was made to it. The error may be associated with the difficulty of completely dehydrating the very granular alumina produced in this way, although ignition over a blow-pipe yielded no better results, or with the formation of a stable carbon–nitrogen compound of the cyanamide type. Whatever the cause, it is worth while emphasizing the error. No difficulty was encountered in the acid treatment.

Aluminum ethoxide distilled at 210–214°C. at 13 mm. and melted at 146–151°C. Analysis gave 16.78 and 16.70 per cent of aluminum; the calculated value is 16.63 per cent. Molecular weight in naphthalene: 631. Calculated molecular weight for $[Al(OEt)_3]_4$: 648.

T	γ	D	P
°C.			
150	13 98	0 919	341 0
165	13 11	0 904	340 9
180	12 24	0 890	340.6
Mean value of P..			340 8

A redetermination on another sample gave mean value of P = 341.5.

Aluminum n-propoxide distilled at 271–275°C. at 14 mm. and melted at 106–108°C. Analysis gave 13.30 per cent of aluminum; the calculated value is 13.21 per cent. Molecular weight in naphthalene: 865. Calculated molecular weight for $[Al(OPr)_3]_4$: 816.

T	γ	D	P
°C.			
110	19.18	0.957	445.9
130	17.92	0.938	447.4
150	16.66	0.921	447.5
Mean value of P...........			446.9

Aluminum isopropoxide distilled at 151–153°C. at 15 mm. and melted at 118°C. Analysis gave 13.20 per cent of aluminum. Molecular weight in naphthalene: 775. Calculated molecular weight for $[Al(OPr)_3]_4$: 816.

T	γ	D	P
°C.			
60	20.28	0.944	458.6
80	18.84	0.926	459.1
100	17.04	0.904	458.3
120	15.68	0.881	460.5
Mean value of P.......			459.1

Aluminum n-butoxide distilled at 274–278°C. at 9 mm. and melted at 102–106°C. Analysis gave 10.98 per cent of aluminum; the calculated value is 10.95 per cent. Molecular weight in naphthalene: 968. Calculated molecular weight for $[Al(OBu)_3]_4$: 984. Molecular weight by boiling point in benzene: 1050. Molecular weight by boiling point in *n*-butyl alcohol: 1025. Electrical conductivity in *n*-butyl alcohol (1 g. in 50 cc.) $< 4 \times 10^{-5}$ mhos.

T	γ	D	P
°C.			
80	20.48	0.925	565.4
100	19.11	0.909	565.7
120	17.69	0.893	565.2
140	16.33	0.875	565.0
Mean value of P.........			565.3

Aluminum isobutoxide distilled at 248–250°C. at 11 mm. and melted at 208–210°C. It exhibited no supercooling. Analysis gave 11.05 per cent of aluminum. Molecular weight in naphthalene: 968.

T	γ	*D*	*P*
°C.			
209	11 84	0 827	551 7
217	11 52	0 819	553 3
Mean value of *P*			552 5

Owing to the high melting point and viscosity and the consequent difficulty of making parachor determinations, great reliance cannot be placed on this result.

Aluminum sec-butoxide distilled at 174–176°C. at 5 mm. It did not solidify even after standing for two months. Analysis gave 10.94 per cent of aluminum. Molecular weight by boiling point in benzene: 994.

T	γ	*D*	*P*
°C.			
50	23 19	0 937	576 4
70	21 49	0 917	577 5
90	19 96	0 894	581 7
110	18 10	0 868	584 8
Mean value of *P*			580 1

Antimony ethoxide was prepared by the interaction of antimony trichloride and sodium ethoxide in absolute alcohol. It distilled smoothly at 99.5°C. at 13 mm. or 95°C. at 11 mm., without any sign of ebullition, to a colorless liquid. Molecular weight in naphthalene: 302. Calculated molecular weight for $Sb(OEt)_3$: 257.

T	γ	*D*	*P*
°C.			
17	28 36	1 524	389 0
37	26 58	1 490	391 2
57	24 77	1 455	393 6
77	23.16	1 420	396 7
130	17 66	1 328	396 4
150	16 18	1 295	397 4
170	14 53	1 262	397.3
190	12 87	1 229	395 9
Mean value of *P* (77–190°C.)			396.7

DISCUSSION

The unsuitability of the alkyl oxides as a means of determining the parachor of aluminum (*vide infra*) necessitates the tentative acceptance of the value derived from chelated compounds. This has now been confirmed by measurements on the acetylacetonate and new measurements on the ethyl acetoacetate and the diethylmalonate, from which, assigning singlet linkage formulations to these compounds, values of 43.9, 41.4, and 36.0, respectively, are obtained for the parachor of aluminum. The latter value is probably somewhat erroneous because it is derived from a large molecular parachor, but taking the mean of these three values together with the three values of the parachor given by Sugden (9), a figure of 39.5 results for the parachor of aluminum.

This value may be checked by taking the parachor of chromium as 53.7 from the data for chromyl chloride (2) and comparing the acetylacetonates of chromium and aluminum which are found to differ in their parachors by 16.3 units. It then follows that the parachor of aluminum is 37.4. This fixes the order of the atomic parachor independent of the validity of the singlet linkage formulation of the acetylacetonate.

TABLE 1

Comparison between observed parachors of alkyl oxides and those calculated for the formula, $Al(OR)_3$

OXIDE	*P* (OBSERVED)	*P* (CALCULATED)	ANOMALY
Ethoxide	340.8	384.8	−44.0
n-Propoxide	446.6	501.8	−55.2
Isopropoxide	459.1	501.8	−42.7
n-Butoxide	565.3	618.8	−53.5
Isobutoxide	552.5	618.8	−66.3
sec-Butoxide	580.1	618.8	−38.7

Assuming the value of 39.5 for the parachor of aluminum obtained with the aid of singlet linkage formulations, a comparison can be made between the observed parachors of the alkyl oxides and those calculated for the simple formula, $Al(OR)_3$, as shown in table 1.

The hypothesis that the liquids have an angle of contact which would reduce the apparent surface tension can be shown to be an inadequate explanation, since an angle of contact of at least 60° would be necessary to account for the anomalies and such an angle would have been easily detected in the microscope. In every case the meniscus was normal.

Molecular weight determinations from the freezing point of naphthalene solutions and the boiling point of benzene and *n*-butyl alcohol solutions showed that the molecules are polymerized fourfold in solution, and since the parachor was constant over a considerable temperature range (except in the case of the *sec*-butoxide), it is probable that any polymerization which occurs in the pure liquid is not affected by temperature. Application of the Ramsay–Shields equation to the surface tension data favors the simple formula $Al(OR)_3$, but the validity of this equation may be questioned. It was hoped to obtain conclusive evidence on this point by a vapor density determination under reduced pressure with the apparatus previously described (5), but, although excellent results could be obtained with other compounds, some decomposition always occurred with these alkyl oxides. This is remarkable in view of the ease with which the compounds could be distilled without decomposition, but all attempts to vaporize them in the Victor Meyer tube resulted in decomposition, although vaporization was carried out under a variety of conditions. The results, however, are not entirely without significance because in whatever way decomposition occurs, e.g.,

$$2Al(OEt)_3 \rightarrow Al_2O_3 + 3Et_2O$$

or

$$2Al(OEt)_3 \rightarrow Al_2O_3 + 3H_2O + 6C_2H_4$$

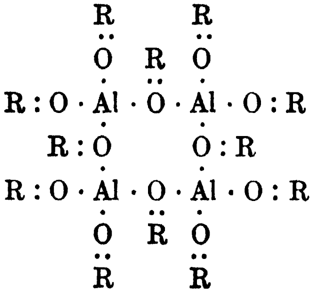
the number of molecules produced by decomposition must be larger than the number of alkyl oxide molecules even if these are unpolymerized. Thus decomposition would lower the apparent molecular weight. The observed molecular weights were with one exception larger than those calculated from the simple formula, and in the single case in which agreement was obtained it was apparent that considerable decomposition had occurred. Vapor density determinations therefore show that polymerization occurs, but afford no estimate of the degree of polymerization.

The balance of evidence is in favor of the formula $[Al(OR)_3]_4$, in which case the compounds are analogous to the thallous alkyl oxides which Sidgwick and Sutton (7) have shown to be tetramolecular in alcohol and benzene solution but which, surprisingly, give a normal value for the parachor of thallium (9). The parachor anomaly of the aluminum alkyl oxides is paralleled to a lesser extent in antimony ethoxide, which presents the phenomenon of an increasing parachor at low temperatures (presumably due to slight polymerization), followed by a constant parachor at higher temperatures. This constant parachor, which indicates complete depolymerization, falls short of that calculated from the known parachor of antimony by 14 units. Germanium ethoxide also exhibits a deficiency of seven units (6). Methyl and ethyl orthosilicates have parachors increasing with temperature (10), differences of approximately 5.3 and 6.3 units being observed over a 54°C. range. The boron esters are normal (1).

The formula $[Al(OR)_3]_4$ would bring these compounds into line with the "alkoxo salts" of Meerwein and Bersin (4), if $[Al(OR)_3]_4$ is written

$Al[Al(OR)_4]_3$, but a polar formulation is improbable because the aluminum alkyl oxides, like the "alkexo salts," have the non-polar properties associated with covalent links, e.g., they melt and distil at low temperatures and the *n*-butoxide has a very small conductivity in *n*-butyl alcohol solution.

By analogy with the ring structure assigned by Sidgwick and Sutton (7) to thallous ethoxide, aluminum ethoxide may be written as in formula I,



I

but because of the ring structure in I the parachor anomaly must be raised to 45.8, and a negative anomaly of this magnitude can only be accounted for by four singlet linkages associated with each aluminum atom. A model constructed with the four aluminum bonds arranged tetrahedrally and the Al—O—Al bonds making an angle of 110° shows that a ring structure of this type is practically strainless, although the eight atoms in the ring do not all lie in the same plane. However, although this formulation may be supported on steric grounds, it seems highly improbable that stability can be attained with only four electrons in the valency shell of each aluminum atom and five unshared electrons to each oxygen atom.

A further difficulty is encountered in the fact that larger negative anomalies are found in the higher alkyl oxides of aluminum. This is not peculiar to this series of homologues. Thus the parachor of beryllium propionylacetonate is higher than that of the acetylacetonate by 68.6 (calculated, 78), while the difference between the parachors of acetyl- and propionylacetone is 34.3 (calculated, 39), and that between sulfonal and trional is only 28.3 units.

SUMMARY

1. Aluminum alkyl oxides have been prepared from ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *secondary*-butyl alcohols; also prepared were the acetylacetonates of chromium and aluminum, alumino ethyl acetoacetate, alumino diethylmalonate, and antimony ethoxide.

2. Molecular weight determinations indicate a fourfold polymerization of the alkyl oxides of aluminum, which is supported qualitatively by vapor density measurements.

3. Antimony ethoxide with a normal molecular weight exhibits a parachor deficiency of 14 units, deficiencies also being found in the ethoxides of silicon and germanium. The parachor deficiency found in the aluminum alkyl oxides is of a larger magnitude and varies with the nature of the alkyl group. The only reasonable formulation of these compounds which will account for these deficiencies by means of singlet linkages consists of an eight-membered ring with all the oxygen atoms attached to the aluminum atoms by singlet linkages. In this formulation the electron octets of all the atoms are filled with the exception of those of the aluminum atoms, which only possess four electrons each.

We wish to acknowledge the valuable assistance rendered by Mr. W. S. Rapson, M.Sc., in the preparation of many of the compounds used in this investigation.

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NOTES ON ACETYLMETHYLCARBINOL

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The N. V. Nederlandsche Gist-en Spiritusfabriek, Delft, Holland, has recently marketed acetylmethylcarbinol or acetoin, $CH_3 \cdot CO \cdot CH(OH)CH_3$, a slightly yellow liquid which changes spontaneously into a white crystalline polymer. The authors have to thank the above company for a sample of acetoin, which they have examined briefly, since the literature (1, 2, 3, 4, 5) indicates that the polymerization is incompletely understood.

The authors' samples of acetoin were obtained by melting or distilling the original solid polymer. Samples were kept at various temperatures, portions were withdrawn from time to time, and the refractive indexes were determined at 20°C.; typical results are given in tables 1 and 2. The initial value of n varied with the conditions of melting or distilling; the minimum may be 1.4175. At 100°C. and 130°C. the acetoin became browner and more viscous and developed a "burnt sugar" odor. Evidently molecular complexity (polymerization) occurs on keeping the liquid acetoin; the polymer however does not accumulate in the liquid, but forms the solid polymer.

Acetoin, kept in an open beaker in the air, absorbed water; n fell from 1.4186 to 1.4141 in five days. When acetoin was kept over sulfuric acid, the value of n rose to 1.4435 in seven days, but the acetoin volatilized into the acid, darkened it, and formed a substance of sharp odor.

The densities and viscosities of acetoin kept at 30.0°C. were determined, and the results are given in table 2. These properties varied similarly to the refractive index, but to a greater degree. By extrapolation, the freshly distilled acetoin would have $d_{4°}^{30°} = 0.9860$ and $\eta^{30°} = 0.0175$. The density of acetoin is lowered (by about 9 parts in 1000) after boiling, i.e., depolymerization occurs on heating.

The normal freezing point of acetoin was at −72°C., i.e., it repeatedly froze and melted at this temperature. The following vapor pressures of acetoin were found by the static method: 162 mm. at 0°C.; 164 at 10°C.; 168 at 20°C.; 174 at 30°C.; 183 at 40°C.; 210 at 60°C.; 256 at 80°C.; 330 at 100°C.; 449 at 120°C.; 664 at 140°C.; 760 at 144°C.

At ordinary temperatures the acetoin deposited crystals of the polymer in from two to nine days. The polymer was slightly soluble in water, methyl and ethyl alcohols, cyclohexanol, acetone, ethyl acetate, acetic acid, and paraldehyde, and sparingly soluble in ether, benzene, carbon tetrachloride, ethylene bromide, bromoform, and acetophenone. The

TABLE 1

The change of refractive index, $n_D^{30°}$, *of acetoin with time*

AGE OF SAMPLE	REFRACTIVE INDEX, $n_D^{30°}$, OF SAMPLES OF ACETOIN				
	Distilled sample 2 at −10°C.	Melted sample 1 at room temperature	Melted sample 2 at 30°C	Melted sample 3 at 100°C.	Melted sample 4 at 130°C.
days					
0	1.4192	1.4178	1.4184	1.4186	1.4186
1		1.4191	1.4203	1.4198	1.4247
2		1.4202	1.4199	1.4211	Cooled
3		1.4205*	1.4202		1.4278
4	1.4187*	1.4207*		1.4254	1.4421
5		1.4208*	1.4201	1.4278	1.4546
6			1.4200	1.4312	1.4762
7	1.4190*	1.4205*	1.4204	1.4328	
15			1.4200	1.4471	
20	1.4199*		1.4201		

* Denotes that crystals are present in the sample.

TABLE 2

The change of properties of acetoin when kept at 30°C.

AGE OF SAMPLE	MELTED SAMPLE 2	DISTILLED SAMPLE 1		DISTILLED SAMPLE 2		
	$d_{4°}^{30°}$	$d_{4°}^{30°}$	$\eta^{30°}$	$d_{4°}^{30°}$	$\eta^{30°}$	$n_D^{30°}$
1 hr.	0.9889	0.9861	0.0178	0.9865	0.0180	
2¾ hrs.				0.9878	0.0187	1.4192
21 hrs.	0.9949		0.0208	0.9930	0.0207	
26 hrs.				0.9934	0.0209	1.4198
50 hrs.	0.9950		0.0211	0.9938	0.0211	1.4200
4 days			0.0212	0.9938	0.0211	1.4199
5 days	0.9950					
6 days		0.9944	0.0213	0.9939	0.0212	1.4201
7 days	0.99515					
12 days	0.99515					
16 days	0.9952					1.4198
29 days						1.4205

polymer was appreciably volatile at room temperatures; if it held traces of liquid acetoin, it liquefied and volatilized more rapidly. The pure well-crystallized polymer may be kept unchanged for several months, either in closed vessels or between watch-glasses. The crystals are flat, monoclinic, transparent prisms, smooth and greasy to the touch, and of density 1.26.

Many melting-point determinations were done on this polymer. The crystals tended to become opaque at 60–110°C., and they melted at 110–128°C., and in rare cases at 150–160°C.; the general melting point was about 124°C. The crystals also sublimed rapidly at 150–160°C., and less rapidly at 100°C. and lower temperatures. The melting point depended on the rate of heating, on the time the sample was held at a given temperature, and on the use of an open or closed tube; the results hint that a chemical change (polymer → liquid) is involved. This polymer then has no simple or definite melting point; it passes to liquid acetoin at any temperature above 30°C., and perhaps at lower temperatures, in longer or shorter times.

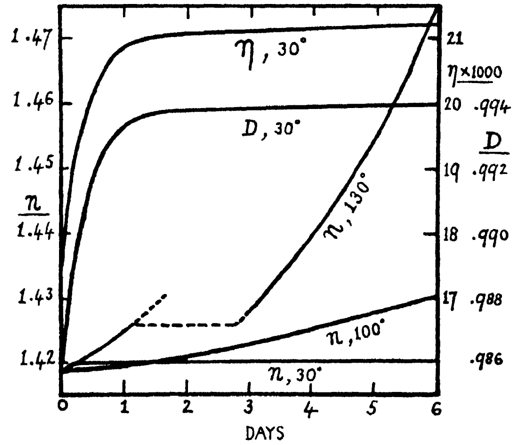

FIG. 1

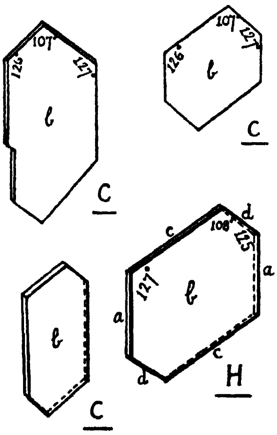

FIG. 2

FIG. 1. VARIATION OF THE PROPERTIES OF ACETOIN WITH TIME

FIG. 2. CRYSTALS OF THE POLYMER OF ACETOIN

By dilatometer experiments the transition temperature between the polymer and liquid acetoin was placed at 16°C.; but in entire absence of the liquid the solid was stable at higher temperatures (*v.s.*).

By the cryoscopic method the polymer was found to be monomolecular in water, acetic acid, and paraldehyde.

In contact with zinc at −10° to 0°C. acetoin became solid within twenty-four hours; the crystals appeared to be the same as before, and they too were monomolecular in the above solvents.

Acetoin was kept by itself for eighteen days at temperatures between −20° and 0°C.; crystals appeared on the fourth day, and about one-third of the sample had crystallized at the last. These crystals, C, had the same form and density as the polymer, H, deposited at room temperatures.

The authors thank Mr. Yates for the following notes and figure 2 about these crystals:—"Three crystals of each substance, C and H, were sketched as seen under the microscope, and their angles on the clino-pinacoidal face were measured. All the crystals were practically identical; they had tabular habit, being very thin in the direction perpendicular to the clino-pinacoidal face, b; their interfacial angles were similar; the symmetry was monoclinic, though the departure from rhombic symmetry was only about 1°. The ortho- and basal-pinacoid faces are a and c, and d is the orthodome face."

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STUDIES ON ORGANIC DEPOLARIZERS[1]

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Determinations of single potentials of cathodes against organic depolarizers made by Hunter and Wernlund (8) as a preliminary to comparing electrolytic reductions of organic compounds with those carried out by chemical reagents showed that the order of the cathodes used, based on their single potentials, was essentially the same with different depolarizers. The present work extended these measurements using the electrodes platinum, nickel, gold, silver, and tin. The results obtained agree with those of Hunter and Wernlund and have led to a further simplification of the theory of depolarization values by including the idea of the "electron affinity" of the depolarizer.

Physicists have made a very thorough study of the emission of electrons into gases in their work on the photoelectric effect, contact potentials, resonance and ionization potentials, and electron emission from hot bodies. They have made it clear that the emission of electrons by metals into gases involves the performance of work, and that the work required is different for each metal and is greatly influenced by the nature of the gas surrounding the emitting surface. It is thus certain that their values found for the work function can not be transferred without change to aqueous solutions, but it is equally certain that the idea of the work function should be used in a study on organic depolarizers.

When an electrode with no current flowing is placed in a solution containing a depolarizer, which may be defined as anything whose presence causes a cathode to become more positive against a solution than it was before the material was added, electrons will be removed from the electrode by the depolarizer. This will result in a continuous and usually rapid increase in the positiveness of the electrode until equilibrium is reached. The single potential of the cathode with the current turned on passes through a minimum "positive" value, owing to the fact that when a depolarizer molecule takes an electron from the metal it then unites with a hydrogen ion, thus producing a change in the ratio of the depolarizer to its reduction product and resulting in a gradual increase in the potential.

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[1] This article is based upon the thesis of L. F. Stone, submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1927. The manuscript was prepared by the junior author after the death of Dr. Hunter in 1931.—L. I. Smith.

The magnitude of the increased positiveness obtained with any one depolarizer will depend to a large extent on the work required to remove electrons from that cathode or on the work function under the conditions of the experiment. Other effects will have an influence on the actual value of the single potential, but in general their magnitude will be small and will be of the same order with any one depolarizer except insofar as the effects are due to the electrode material. Thus the value of the single potential of a cathode in contact with a given depolarizer will be largely dependent on the work function of that electrode and will therefore vary with different metals. As shown in figure 1 the values of the single potentials of the cathodes in contact with a given depolarizer, such as quinone, become more negative in the following order: platinum, gold, silver, nickel, and tin. The values of the work function of these electrodes, under the conditions of our experiments, increase in the same order.

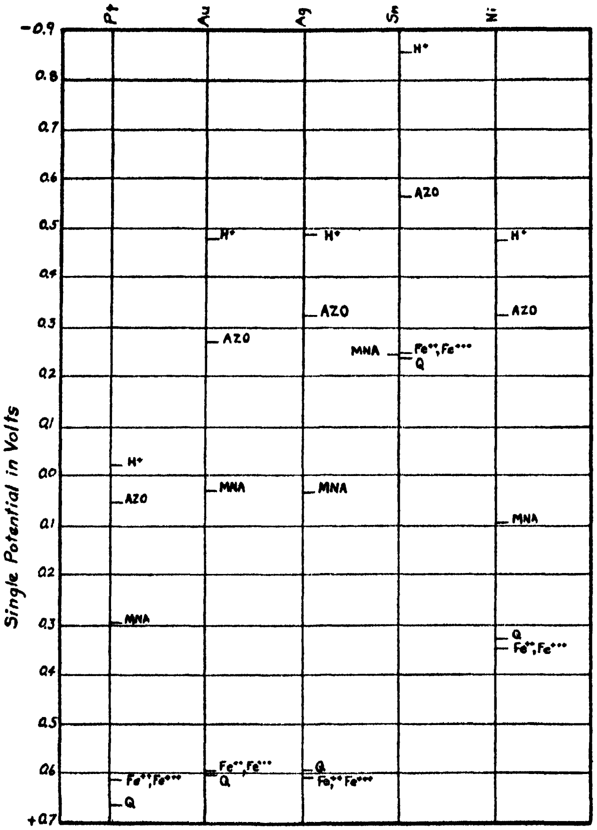

FIG. 1. SINGLE POTENTIALS OF CATHODES AGAINST DIFFERENT DEPOLARIZERS

The values of the single potentials of nickel and tin are often complicated, owing to the fact that in the presence of some depolarizers these cathodes become sufficiently positive to send their ions into solution. When a tin electrode, for example, is placed in a depolarizer solution, some of the electrons will be removed and the force holding the tin ions in the metal therefore becomes less. As the normal potential of the electrode is approached, this force is overcome and metal ions enter the solution. The potential will then remain close to the value of the normal potential for tin, the actual value depending on the number of ions sent into the solution as well as on the depolarizer and its reduction products. Solution of metal ions will occur with any electrode that is in contact with a depolarizer that has a sufficient force of attraction for electrons, or "electron affinity," to reduce the potential of the electrode to its normal potential against its own ions. The effect of the work function thus appears to be masked to some extent in these cases, owing to the introduction of a new depolarizer,—the metal ion.

In determining the single potential of a cathode against various depolarizers it will be found that some of the latter decrease the potential very slightly, while with others the effect is very marked. Every depolarizer will have a definite potential with a given cathode, and that position will be determined by the electron affinity of that depolarizer. It is well known that the potential of a pure substance has an infinite value and will not give the "definite potential" noted above except when a finite quantity of the reduced material is also present, and the value under these conditions will be dependent upon the ratio of the concentration of the depolarizer to its reduction product.

The value of the electron affinity of any one depolarizer depends on two parts of the molecule: the "characteristic group," which is that part of the compound that takes up electrons from the cathode, and the rest of the depolarizer molecule. Different groups vary considerably in their force of attraction for electrons, while the rest of the compound has very little effect on the single potential and probably exerts its influence only through the characteristic group. The difference between the single potentials of nitrobenzene and nitrosobenzene, for example, would be much larger than that between nitrobenzene and *m*-nitroaniline.

Although the actual values of electron affinity can not be determined, we believe that relative values for different depolarizers can be deduced from a study of the data obtained in our experiments. The values of the single potentials obtained in our work with different depolarizers against the cathodes platinum, gold, silver, nickel, and tin are given in figures 1 and 2. The values of the single potentials of several of the depolarizers against platinum, given in figure 2, were obtained from data given by other investigators. The single potential values of formaldehyde, acetaldehyde, pyridine, and acetone were obtained from the work carried out by Hunter and Wernlund (8) under conditions identical with those of the present work. The values for I^-, I_2 (solid) given by Thompson (11) and those for OH^-, O_2; Br^-, Br_2 (liquid); Cl^-, Cl_2 (gas); and F^-, F_2 (gas) given by MacDougall (9) were obtained in studies in which there was no external electromotive force impressed on the cell, and are therefore slightly more positive than they would be under the conditions of our experiments.

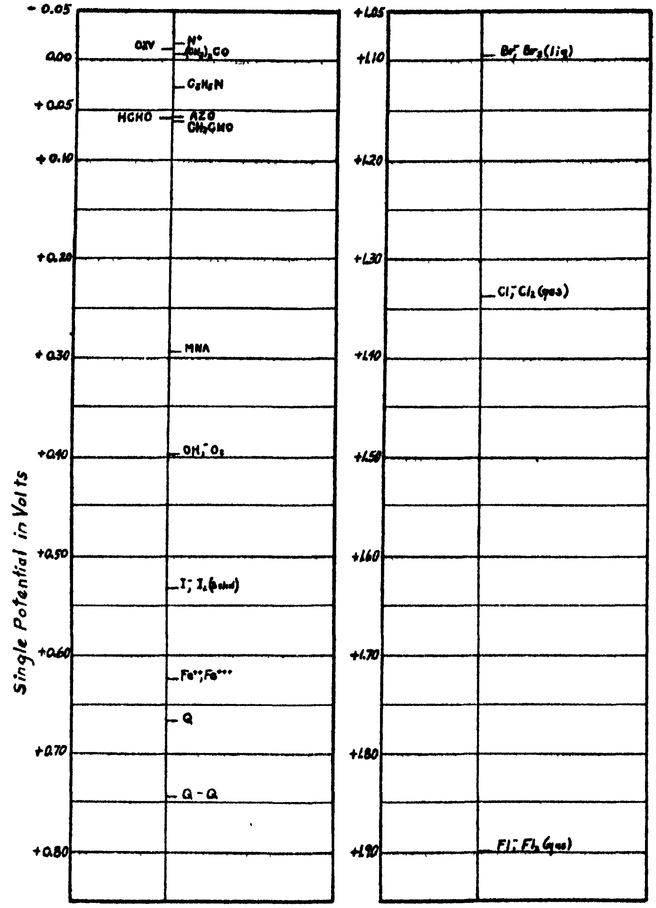

FIG. 2. SINGLE POTENTIALS OF PLATINUM AGAINST DIFFERENT DEPOLARIZERS

In figure 1 it may be seen that the depolarizers tested against gold, in the order of decreasing positiveness of single potential, are as follows: quinone; ferro–ferri; *m*-nitroaniline; azobenzenesulfonic acid; and hydrogen ion. On the basis of our theory the relative values of the electron affinity of these depolarizers decrease in the same order. This order of the depolarizers is the same as that obtained on the other electrodes with the exception of three points. In these cases the difference in the values is very small and may well be due to other effects not considered by us.

Assuming that all cations present in a catholyte may be considered as depolarizers brings the concept of hydrogen overvoltage into accord with our general picture of cathodic action. Thus, the single potential of quinone against the cathodes tested becomes more negative in the order: platinum, gold, silver, nickel, and tin. This is also the order of the metals against the hydrogen ion. In the latter case the actual value of the single potential on a given cathode is probably not dependent on the electron affinity of the depolarizer alone but also on other effects, such as adsorption of hydrogen into the metal and gas films. The failure of the hydrogen discharge point to "space" as well as other depolarizers as regards their distances on the scale of potentials given in figure 1 may well be due to these latter, acting not as primary causes of overvoltage but as secondary effects superimposed on that of electron affinity. It therefore seems possible to speak of the overvoltage of any depolarizer as well as of hydrogen and with the same meaning,—the increase of potential necessary to discharge it on a given cathode over and above that required on platinum.

It thus appears that the "electron affinity" of the depolarizer and the "work function" of the electrode are definite properties of the depolarizer and electrode, respectively, and that it should be possible to estimate the single potential of a depolarizer on a given cathode when its value on platinum is known. Although the present work did not include the formulation of an equation for calculating the electromotive force of a cell, we believe that an equation, perhaps of the Nernst type, should also include other terms that are a function of the "electron affinity" of the depolarizer and the "work function" of the electrode.

EXPERIMENTAL

Electrodes

All electrodes were 3.8 cm. in diameter and 1.5 mm. in thickness. Gold electrodes made from sheet metal, 99.99 per cent pure, were plated using the solution given by Blum and Hogaboom (1). The silver electrode made from sheet silver, 99.99 per cent pure, was plated using the solution given by Blum and Hogaboom (2). Platinum electrodes made from sheet platinum were plated using the bath recommended by Findlay (7). Tin electrodes containing 99.97 per cent tin and 0.03 per cent lead were plated using the solution given by Blum and Hogaboom (3). Nickel electrodes, prepared from electrolytic nickel, were plated using the solution recommended by Blum and Hogaboom (4).

Depolarizers

Quinone, prepared from hydroquinone by the method given by Vliet (12), was recrystallized from benzene and sublimed twice. A fresh 0.015

molar solution in 2 *N* sulfuric acid was made for each run. Twenty-five grams of *m*-nitroaniline, m.p. 112.5°C. after recrystallization twice from water, was treated with 10 cc. of concentrated sulfuric acid to form the sulfate, and dissolved in 2 *N* sulfuric acid to give the 0.181 molar solution used in the experiments. The ferrous–ferric solutions, having a ratio of 1:1, were made from Merck's Blue Label iron sulfates. Azobenzenesulfonic acid, prepared from azobenzene, was recrystallized from water and dissolved in 2 *N* sulfuric acid to give a 0.01 molar solution. 3,3′-Diaminoazoxybenzene, m.p. 145–147°C., made from *m*-nitroaniline according to the procedure given by Meldola and Andrews (10), was recrystallized from alcohol, and a 0.002 molar solution in 2 *N* sulfuric acid was made for use in the runs on platinum.

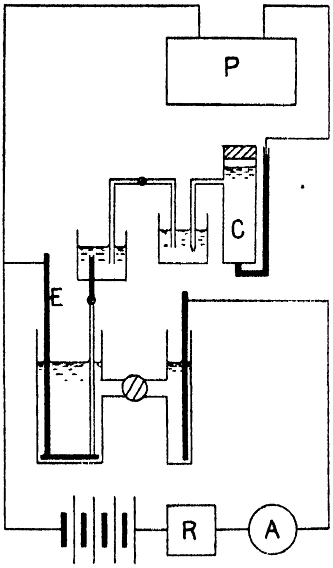

Fig. 3. The Apparatus

Apparatus (see fig. 3)

The cathode chamber of the cell was 10 cm. in height and 4.5 cm. in diameter, and was separated from the anode chamber by a stopcock. Current from the storage batteries, used to impress an external electromotive force on the cell, was regulated by a resistance box (R) and was measured by a milliammeter (A). The cathode (E) was connected to a Leeds and Northrup type K potentiometer (P) and the cell completed by the calomel electrode (C), salt bridge, and capillary tube. The calomel electrodes, prepared from distilled mercury, fresh calomel, and a saturated solution of recrystallized Merck's Blue Label potassium chloride, were frequently checked against each other and showed variations of the order of 0.1 to 0.05 millivolt.

Typical runs

In method A 75 cc. of 2 *N* sulfuric acid was added to the cell after all connections were made. A constant current of 50 milliamperes was passed through the cell and readings taken, constant stirring being maintained by means of an electrically driven glass stirrer. The stopcock separating the chambers was then closed and 50 cc. of the 2 *N* sulfuric acid in the cathode chamber was replaced with 50 cc. of a depolarizer solution. The stopcock was then opened and readings again taken. In method B the depolarizer solution was added to the cell, and readings taken before and after turning on the current of 50 milliamperes.

TABLE 1

Results obtained with the depolarizers m-nitroaniline, 3,3′-diaminoazoxybenzene, quinhydrone, and hydrogen ion

ELECTRODE MATERIAL	DEPOLARIZER IN 2 N H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	M.N.A.	A	0.3012^{+}	
Platinum	M.N.A.	B	0.2889^{+}	
Gold	M.N.A.	A	0.0467^{+}	
Gold	M.N.A.	B	0.0162^{+}	
Silver	M.N.A.	A	0.0404^{+}	
Silver	M.N.A.	B	0.0272^{+}	
Tin	M.N.A.	A	0.2441^{-}	
Tin	M.N.A.	B	0.2451^{-}	0.2101^{-}
Nickel	M.N.A.	A	0.1020^{+}	
Nickel	M.N.A.	B	0.0964^{+}	0.2276^{+}
Platinum	Oxy	B	0.0116^{-}	
Platinum	Quinhydrone*			0.6970^{+}
Platinum	2 N H_2SO_4†	B	0.0212^{-}	
Gold	2 N H_2SO_4	B	0.4752^{-}	
Silver	2 N H_2SO_4	B	0.4889^{-}	
Tin	2 N H_2SO_4	B	0.8642^{-}	
Nickel	2 N H_2SO_4	B	0.4738^{-}	

* Saturated solution.

† Data given are the average of the final, nearly constant values determined over a period of three to four hours.

Preliminary runs indicated that the values of the single potentials of the electrodes in contact with the various depolarizers passed through the minimum "positive" value noted above, and were becoming more negative very slowly, approximately five minutes after the addition of the depolarizer, in the case of method A, and five minutes after the current of 50

TABLE 2

Results obtained with the depolarizers quinone, ferro–ferri, and Sn^{++}

ELECTRODE MATERIAL	DEPOLARIZER IN 2 N H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	Quinone	B	0.6703^+	
Gold	Quinone	B	0.6045^+	0.7804^+
Silver	Quinone	B	0.5925^+	0.6481^+
Tin*	Quinone	B	0.2363^-	0.2063^-
Nickel†	Quinone	B	0.3268^+	0.3569^+
Platinum	Fe^{++}–Fe^{+++}	A	0.6197^+	
Platinum	Fe^{++}–Fe^{+++}	B	0.6244^+	0.6684^+
Gold	Fe^{++}–Fe^{+++}	A	0.5938^+	
Gold	Fe^{++}–Fe^{+++}	B	0.5965^+	0.6666^+
Silver	Fe^{++}–Fe^{+++}	A	0.6073^+	
Silver	Fe^{++}–Fe^{+++}	B	0.6159^+	0.6604^+
Tin*	Fe^{++}–Fe^{+++}	A	0.2488^-	
Tin*	Fe^{++}–Fe^{+++}	B	0.2482^-	0.2067^-
Nickel†	Fe^{++}–Fe^{+++}	A	0.3418^+	
Nickel†	Fe^{++}–Fe^{+++}	B	0.3491^+	0.3797^+
Tin	Sn^{++}‡	B	0.2348^-	0.2036^-

* A positive test for tin ions in the solution was obtained at the end of the run.

† A positive test for nickel ions in the solution was obtained at the end of the run.

‡ Molar solution of tin ions.

TABLE 3

Results obtained with the depolarizers azobenzenesulfonic acid and quinone–quinhydrone

ELECTRODE MATERIAL	DEPOLARIZER IN 2 N H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	Azo	B	0.0584^+	
Gold	Azo	B	0.2745^-	
Silver	Azo	B	0.3203^-	
Tin*	Azo	B	0.5729^-	
Nickel†	Azo	B	0.3273^-	
Platinum	Q–Q‡			0.7452^+
Gold	Q–Q			0.7433^+
Silver	Q–Q			0.6792^+
Nickel	Q–Q			0.3517^+
Tin	Q–Q			0.1994^-

* A negative test for tin ions in the solution was obtained at the end of the run.

† A negative test for nickel ions in the solution was obtained at the end of the run.

‡ Saturated solution quinone–quinhydrone. Constant values for the platinum and gold electrodes were reached in about five minutes. An initial value of 0.6552 was obtained for silver, the final constant value of 0.6792 being reached in about two hours. The value for the nickel electrode was not constant, probably owing to the complexity of the solution. The value given for the tin electrode was fairly constant. Tests on the solutions in contact with the latter two electrodes showed the presence of nickel and tin ions, respectively.

milliamperes was turned on, in the case of method B. All of the values given in the tables are based on readings taken five minutes after the start of the run. These readings were corrected to 25°C. and 760 mm., using the data given by Fales and Mudge (6). These corrected values were reduced to the normal hydrogen scale (E_h) by adding algebraically $+0.2464$, the value given by Clark (5) for the saturated calomel electrode, referred to the normal hydrogen electrode at 0°C. Although readings were taken to four places, the true value is not certain closer than a few millivolts when measurements are made during reduction.

Tables

The data obtained on the cathodes against the various depolarizers tested are given in tables 1, 2, and 3, and in figures 1 and 2. Abbreviations used are as follows: azo = azobenzenesulfonic acid; oxy = 3,3′-diaminoazoxybenzene; M.N.A. = *m*-nitroaniline; Q = quinone; Q–Q = quinone–quinhydrone.

SUMMARY

1. The single potentials of several depolarizers have been measured against different cathodes.

2. The idea of the "work function" of electrodes has been developed as applied to electrolytic action, and the variation of its value with different metals has been explained.

3. The "electron affinity" of depolarizers has been defined and its function discussed.

4. A new view of "overvoltage" has been developed along the lines indicated by our theory.

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EQUILIBRIUM DISTRIBUTION OF ACETIC ACID BETWEEN ISOPROPYL ETHER AND WATER

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The removal of undesirable constituents or the recovery of valuable components from solution by selective extraction with non-miscible solvents is a potentially important chemical engineering operation for which few significant quantitative data are available. In the course of experimental studies of the rate of extraction of acetic acid from aqueous solution by isopropyl ether, comprising one phase of an extensive program of investigation of the rates of liquid–liquid extraction processes in progress in the Department of Chemical Engineering of Princeton University, it became necessary to have available distribution data for this system. Inasmuch as the literature apparently reveals no published measurements of this distribution equilibrium, our data on it are presented in this paper. As this system is the basis of a commercial process for the recovery of acetic acid from aqueous solution by extraction, these results are of industrial as well as academic interest.

EXPERIMENTAL TECHNIQUE

Material. The measurements were made with purified isopropyl ether from the Eastman Kodak Company and with distilled water as the solvents, and also with technical isopropyl ether obtained directly from the Carbide and Carbon Chemicals Corporation and with the local tap water. The technical ether was dry to anhydrous copper sulfate, contained an acidity less than 0.01 per cent, and less than 3 per cent by weight of isopropyl alcohol. The acetic acid was glacial (99.5 per cent) acid of the U.S.P. grade.

Analytical method. Acetic acid concentrations in both water and ether phases were determined volumetrically by titration of 10-cc. to 25-cc. samples with a standard alcohol solution of sodium hydroxide. This was prepared by dissolving the usual purified stick caustic in 95 per cent ethyl alcohol, standardized against constant-boiling hydrochloric acid, and employed in concentrations of 0.1 *N*, 0.5 *N*, and 1.0 *N* according to the concentration range in the system under investigation. Prior to titration the samples were diluted to three times the original volume to insure complete miscibility with the titrating solution, alcohol acting as a common solvent. The indicator was phenolphthalein.

Procedure. The distribution measurements were carried out by the ordinary laboratory method usually employed for this purpose. The two solvents, water and isopropyl ether, one containing a sufficient quantity of acetic acid to produce the final acid concentration range desired, were placed in 250-cc. glass-stoppered bottles. The volume of each solvent was usually 100 cc. In order to approach the equilibrium from both sides and thus minimize possible error due to failure to attain equilibrium, independent series of experiments were conducted with acetic acid initially in the water phase and in the ether phase, respectively. After sealing, the bottles were vigorously agitated, placed in a thermostat at 20 ± 0.5°C., and allowed to remain for a period of 170 hours with vigorous agitation at frequent intervals. Ten-cc. samples from each layer were analyzed for acid after 48 hours and 25-cc. samples at the end of 170 hours. Inasmuch as the analyses of the two sets of samples checked closely, it was assumed that equilibrium had been attained. Precaution was taken to prevent evaporation of ether from the samples, these being run directly into alcohol in stoppered flasks. As a check, the sum of the quantities of acid found in each layer by the analyses was compared with the known total quantity of acid originally added to the system. Duplicate experiments were performed for the majority of concentrations.

EXPERIMENTAL RESULTS

The results of the measurements for various acid concentrations are listed in table 1. In this table equilibrium concentrations, expressed in gram-moles per liter of solution, for the water, C_w, and ether, C_e, phases are given in columns 1 and 2, respectively. Corresponding values of the apparent distribution coefficient, $D_{\text{obsd.}} = C_e/C_w$, calculated from the observed concentration on the assumption that the simple ideal distribution law for single undissociated molecules is obeyed, are given in column 3.

It is evident from the data of table 1 that the ideal distribution law is only approximately obeyed, inasmuch as the apparent distribution coefficient calculated from the ratio C_e/C_w slowly increases with total acid concentration. This is an expected result, since one is undoubtedly not dealing with a single molecular species in both phases, acetic acid probably undergoing increasing dissociation in the aqueous phase with increasing dilution and association in the ether phase.

Especially at the higher concentrations the apparent values of the coefficient where the acid was initially in the ether phase are consistently somewhat higher than for corresponding concentrations where the acid was present initially in the water phase. This apparently indicates that true equilibrium was not entirely attained. However, analyses of both phases in each experiment over a 170-hour period with frequent agitation gave no further detectable change in observed concentrations; consequently, further possible change toward equilibrium would be infinitely slow. The apparent variation from true equilibrium is less significant than at first appears, and is probably within the limits of possible analytical error. A deviation in the observed concentrations from the true equilibrium values is multiplied twofold in the calculation of the distribution ratio, and, furthermore, an average error of 0.02 to 0.05 cc. in the titration value could account for the minor discrepancies obtained.

TABLE 1

Distribution of acetic acid between water and isopropyl ether at 20°C.

EQUILIBRIUM CONCENTRATION IN GRAM-MOLES PER LITER		DISTRIBUTION COEFFICIENT, $D = C_e/C_w$	
Ether, C_e	Water, C_w	Observed	Calculated from equation 3
(a) Pure ether and distilled water			
0.0136	0.0732	0.185	0.180
0.0140*	0.0785	0.178	0.180
0.0254	0.1450	0.177	0.182
0.0560*	0.2980	0.188	0.186
0.0577	0.3030	0.190	0.187
0.1186	0.6025	0.196	0.194
0.1430*	0.6925	0.206	0.197
0.1733	0.8900	0.196	0.202
0.2290*	1.1070	0.207	0.208
0.2803	1.3600	0.206	0.215
0.3260*	1.4300	0.228	0.217
0.3994	1.7970	0.222	0.226
0.6740	2.7800	0.242	0.253
(b) Technical ether and tap water			
0.0543	0.2960	0.200	
0.1480	0.7720	0.192	
0.2740	1.3450	0.232	

*In these experiments acid was added initially to the ether.

The results with tap water and technical isopropyl ether are slightly higher than those for the pure solvents. This is probably to be accounted for mainly on the basis of the isopropyl alcohol present in the technical ether.

In figure 1 is plotted the actual distribution equilibrium curve for the range investigated. Distribution data have usually been represented by an empirical equation of the form

$$D' = C_e/C_w^n$$

The present equilibrium curve may be approximately represented over the concentration range investigated by such a parabolic equation, since a satisfactory straight line is obtained in a log-log plot of C_e against C_w. The slope of this line is $a = 1.09$, and its intercept, $D' = 0.148$. Therefore

$$C_e/C_w^{1.09} = 0.148 \qquad (1)$$

which equation may be employed for the approximate calculation of the distribution of acetic acid between water and isopropyl ether over the present concentration range.

DISCUSSION

It has been pointed out by Almquist (1) that the apparent distribution coefficient may frequently be expressed most accurately as a function of the concentration in the water phase by a simple linear equation of the form

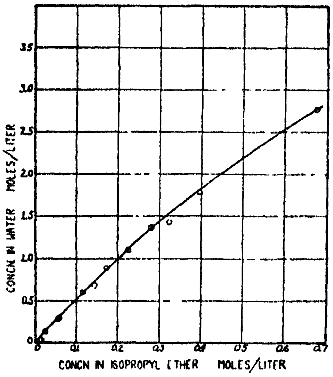

FIG. 1

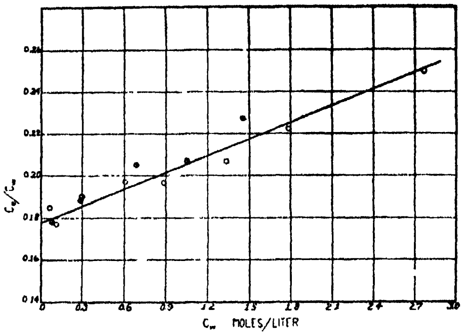

FIG. 2

FIG. 1. EQUILIBRIUM CURVE FOR THE DISTRIBUTION OF ACETIC ACID BETWEEN ISOPROPYL ETHER AND WATER

FIG. 2. VARIATION OF THE APPARENT DISTRIBUTION COEFFICIENT WITH CONCENTRATION IN THE AQUEOUS PHASE

○, acid added initially to the water; ◑, acid added initially to the isopropyl ether.

$$D_{\text{apparent}} = C_e/C_w = D_s\,C_w + D_i \qquad (2)$$

where D_s is the slope and D_i the intercept. Such an equation possesses theoretical significance and supplies an accurate and useful means of recording, testing, and interpolating distribution data. That the data for the present case conform to such an equation may be seen from figure 2, in which a straight line results from a plot of the ratio C_e/C_w against C_w. The slope of this line is 0.027 and its intercept is 0.178. Hence, its equation is

$$D_{\text{apparent}} = C_e/C_w = 0.027C_w + 0.178 \qquad (3)$$

This equation may be employed with considerable accuracy for distribution calculations for acetic acid between water and isopropyl ether and is recommended for this purpose. In column 4 of table 1 values of the apparent coefficient calculated from the concentrations in the water phase by means of equation 3 are given. Since equation 3 is based on the measurements approaching the equilibrium from both sides, thus representing average values, it is probable that the calculated values in column 4 represent the true distribution ratio more accurately than do the individually observed values in column 3.

Based on theoretical considerations involving the possible distribution and association equilibria existing in such a case and assuming no association in the water phase, Almquist (1) has derived, as a general theoretical relation for the distribution of an organic solute between water and an organic solvent, the equation:

$$C_x/C_w = nK_3K_2^nC_w^{n-1} + K_2 \tag{4}$$

In this equation

n = number of molecules in the polymer in the non-aqueous phase.

$K_3 = (A'_n)/(A')^n$ = association constant in the non-aqueous phase, i.e., the equilibrium constant for the reaction $nA' = A'_n$.

$K_2 = A'/A$ = distribution constant for single molecules between the two phases.

A' and A = concentrations of single molecules in the non-aqueous phase x and the water phase w, respectively.

If the solute is mainly associated only into double molecules in the non-aqueous phase, then $n = 2$, equation 4 reduces to

$$C_x/C_w = 2K_3K_2^2C_w + K_2 \tag{5}$$

and the apparent distribution coefficient is a linear function of C_w. Since this is the case for acetic acid between the present solvents, it is evident that acetic acid is associated into double molecules in isopropyl ether over the concentration range investigated. In the present case the slope of equation 3, 0.027, is identical with $2K_3K_2^2$, the slope of equation 5, and the intercept, 0.178, corresponds to K_2. It therefore follows that the value of the distribution constant for single molecules of acetic acid between water and isopropyl ether is $K_2 = 0.178$, and the value of the association constant for acetic acid in isopropyl ether is $K_3 = 0.43$, concentrations being expressed in moles per liter.

At very low concentrations, owing to dissociation in the water phase, and at very high concentrations where association in the water phase may become appreciable, simple relations of the above form may be expected to be no longer valid.

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STUDIES ON SILICIC ACID GELS. V

The Determination of the Hydrogen-Ion Concentration of the Gel Mixtures

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INTRODUCTION

In a recent study in this laboratory, on the time of set of gels of silicic acid, Hurd and Carver (1) have emphasized the importance of the pH of the mixture. The quinhydrone method was used to determine the pH. In the special study of the effect of the pH upon the time of set of these gels, Hurd, Raymond, and Miller (2) have used the quinhydrone method also. In view of the apparent importance of this factor, we have considered it essential to make a very careful study of the applicability and reliability of the quinhydrone method in solutions containing silicic acid.

HISTORICAL

The determination of the pH of a solution containing colloidal material is always attended by a certain amount of uncertainty. When one considers the adsorptive powers possessed by colloidal silicic acid, any method for the determination of the pH may be viewed with considerable suspicion.

The indicator method has been used by several investigators, in particular Prasad and Hattiangadi (3). Their difficulties with this method were that the turbidity of the gel mixture caused difficulty in the determination of the color of the indicator. The alcohol in their indicator solution affected the setting of the gel. Our experiments with the indicator method have substantiated these results, and led us to discard the method where the quinhydrone method could be used, that is, in acid gel mixtures.

The glass electrode–vacuum tube potentiometer method has been used, so far as we know, only to check the quinhydrone method, as mentioned by Hurd and Carver (1). It was used only in acid gels. The results by both methods checked satisfactorily.

The quinhydrone method has been used in the studies made in this laboratory, as mentioned. This method depends upon the fact that quinhydrone introduces equal concentrations of quinone and hydroquinone into the solution. If, in these gel mixtures, the colloidal material present should adsorb or render inactive any appreciable quantity of either the quinone or the hydroquinone, the method would not yield satisfactory results for the pH. On the other hand, if the colloidal material should adsorb only a portion of the quinone and the hydroquinone, but in equimolecular amounts, the method should give reliable results. Also, if the colloidal material should not adsorb any of the quinone or hydroquinone, the results should be accurate. Lastly, there is a possibility that some colloidal silicic acid may be adsorbed onto the platinum wire electrode and so cause an error in the determination.

EXPERIMENTAL

The method of investigation devised was as follows. Standard buffer solutions were prepared, using potassium acid phthalate and sodium hydroxide. Six different gel mixtures were prepared. The gel was washed free from soluble materials, namely the sodium acetate and the acid or base which is in excess. The pH of the buffer solution was determined before and after the addition of different amounts of a suspension of the washed and finely suspended gel in water. No evidence of any change in pH was noted. Blanks were also run, using the same volume of distilled water as was used of the gel suspension. No change in pH was noted.

In each determination, 50 cc. of the buffer solution was used. Solid quinhydrone was added until a slight excess remained undissolved. The pH was measured with a Leeds and Northrup quinhydrone pH indicator #7654. A saturated calomel electrode was used. For the quinhydrone electrode we have used a bright platinum wire in a coil. Such an electrode has given us good results, and is easier to clean than the conventional gold wire electrode. The maximum amount of gel suspension or distilled water added was 20 cc.

The preparation of a washed gel, free from electrolytes, presented considerable difficulty. The method of extracting lumps of the gel with distilled water in several extractions was discarded as being uncertain and requiring too much time. Various filtration methods proved unsatisfactory. The method finally developed was as follows. The solutions of sodium silicate and acetic acid were mixed in a beaker and allowed to set. About three times the volume of distilled water was added and the gel broken into coarse lumps. A small, thin stirrer, driven by a very high speed motor, was used to break up the gel into very fine pieces and mix it completely with the distilled water. The gel was allowed to settle and the supernatant liquid was poured away. This could be done very completely, since after standing for a short time the settled gel seemed to knit itself together into a reasonably firm mass. This fact is interesting and is receiving further study. After this process had been repeated several times, the gel was found to be neutral and free from impurities. It was very essential in this problem that the gel should be entirely free from acid or base. The gel was resuspended in about three times its volume of distilled water before being used.

The data are shown in tables 1 and 2.

The concentration of sodium silicate is expressed as normality in terms of its equivalent of sodium hydroxide. The silicate used was E brand, produced by the Philadelphia Quartz Co[1]. The Na_2O/SiO_2 ratio by weight is 1/3.25.

TABLE 1

Composition of the silicic acid gels

NUMBER OF GEL	0.611 *N* SODIUM SILICATE	2.05 *N* ACETIC ACID
	cc.	*cc.*
1	50	20
2	65	20
3	45	20
4	70	20
5	50	25
6	50	10

TABLE 2

Data for buffer solutions

SOLUTION	0.1 *N* SODIUM HYDROXIDE	0.1 *N* POTASSIUM ACID PHTHALATE	DISTILLED WATER	pH
	cc	*cc.*	*cc.*	
A	0.40	50.0	100.0	3.99
B	17.70	50.0	100.0	4.52
C	29.95	50.0	100.0	5.09
D	39.85	50.0	100.0	5.67
E	45.45	50.0	100.0	5.98

The following combinations were tried, using 50 cc. of the buffer solution and from 0 to 20 cc. of the washed gel or distilled water: A5, A6, B1, B4, B5, C1, C2, C3, C4, D1, D2, D4, E5, and E6. In no case was any change in pH observed. Repetition gave identical results.

We may state, therefore, that silicic acid gel in moderate quantities has no measurable effect upon the pH of phthalate buffer solutions from pH = 4.0 to pH = 6.0 as measured by the quinhydrone method. It would therefore seem reasonable to believe that the silicic acid gel present in gel mixtures will have no measurable effect upon the pH determination by the quinhydrone method, the buffering being accomplished by the acetic acid and sodium acetate present.

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[1] The writers wish to thank the Philadelphia Quartz Co. for the silicate used in this research.

To determine whether or not the platinum electrode used in the quinhydrone determination is affected by usage in these silicic acid gel mixtures, a large number of trials were made. Determinations were made in mixtures of known pH, before and after using the electrode in a silicic acid gel mixture. Various methods of cleaning the electrode were used. The electrode always requires a fraction of a minute to come to equilibrium. No evidence of any effect of the silicic acid on the platinum was found. The electrode may be cleaned with filter paper, or any coating of silica may be loosened by treatment with dilute sodium hydroxide without apparently affecting the electrode.

THE EFFECT OF SETTING OF THE GEL UPON THE pH

Because of the accuracy developed here in the use of the quinhydrone method, we have thought it worth while to ascertain again whether any change occurs, during setting, in the value of the pH. Very careful determinations were run on three gel mixtures, one of pH 4.64, one of 5.01, and the third 5.92. Readings were obtained as soon as possible after mixing and were continued until long after the gel had set. No observable change could be detected in the pH. This agrees with observations in this laboratory, as mentioned by Hurd and Carver (1), and agrees with the observations of Prasad and Hattiangadi (3), who determined the pH with indicators.

THE EFFECT OF QUINHYDRONE ON THE TIME OF SET

It has been our practice to determine the time of set and the pH in two different portions of the same mixture. This practice obviates the possibility that the quinhydrone might affect the time of set indicated for the mixture. It would not be expected, from the results shown by Hurd and Carver (1), that such small amounts of a sparingly soluble organic compound of this type would have any appreciable effect upon the time of set, as determined by the tilted rod method.

A number of determinations have been carried out in acid mixtures over the pH range given in this and other papers of the series, to detect any effect on time of set caused by the introduction of the same amount of quinhydrone as is used in a pH determination. The data are omitted in the interest of economy. The effect can be considered negligible.

SUMMARY

A study has been made of the quinhydrone method for the determination of the pH in silicic acid gel mixtures prepared by mixing solutions of sodium silicate and acetic acid. All gel mixtures were acid. The quinhydrone method was found to give reliable results.

It does not appear that the platinum electrode is affected by the colloidal silicic acid.

A method of preparing washed gel, free from electrolytes, is described.

No change in pH during and for some time after setting could be detected in gel mixtures with pH from 4.62 to 5.92.

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NEW BOOKS

Kolloidchemisches Praktikum. By E. SAUER. 21 x 14 cm.; ix + 112 pp. Berlin: Julius Springer, 1935. Price: 4.50 RM.

This laboratory manual gives detailed directions for 140 experiments illustrating the preparation of colloidal solutions, the investigation of their mechanical, electrical, and optical properties, phenomena at boundaries, the properties of gels and jellies, and the analysis of particle sizes chiefly by elutriation.

The majority of the examples chosen are what may be called standard or classical; a few—e.g., the preparation of cadmium sulfide from the cyanide—are drawn from less familiar sources, while a number of experiments have been devised by the author himself. The directions are concise but clear, and students of average attainments should find no difficulty in carrying them out and in acquiring a fair knowledge of colloidal technique. The intelligent student will also notice the only serious error overlooked by the proof reader: to prepare colloidal sulfur according to Raffo's method he is instructed to drop a solution of sodium *sulfate* into concentrated sulfuric acid; it should of course be sodium thiosulfate.

The author says in the preface: "Only in rare cases will sufficient time be available at the universities for a practical course in colloids extending over a whole semester. It is, however, possible to give a survey of colloid chemistry by using one or two afternoons only during one semester."

EMIL HATSCHEK.

Lehrbuch der physikalischen Chemie. By K. JELLINEK. Band V, Bogen 1–18. 25 x 16 cm.; 288 pp. Stuttgart: F. Enke, 1935. Price: 27 marks.

The first part of the fifth and final volume of this well-known treatise consists, broadly speaking, of three sections with the beginning of a fourth. The first section deals with surface phenomena and colloids, including electroendosmose, cataphoresis, electrocapillary phenomena, and the Brownian movement. Since only eighty pages are devoted to this section, the treatment is often brief, but the mathematical deductions are clearly given and such typical experimental results are quoted as are necessary to illustrate the applications of the theory. The second section (pp. 81–204) deals with homogeneous and heterogeneous reaction velocity, and modern aspects are represented by discussions of the work of Hinshelwood, Moelwyn-Hughes, and Brönsted. A good feature is the detailed consideration of typical cases, and the rather involved theory is carefully explained. The section on heterogeneous systems includes activated adsorption. The theory of supersaturated solutions on p. 160 is given without mentioning the names of the authors, Jones and Partington. The third section deals with aspects of electrolysis falling within the range of the volume and includes a discussion of modern research on overvoltage. The section on the structure of matter, with which the fifth volume will mainly be concerned, is introduced by eighteen pages on the determination of the electronic charge.

The present volume, although perhaps less detailed than the preceding ones, is planned and executed on the same lines, and it may be recommended as a clear and able exposition of the subjects dealt with.

J. R. PARTINGTON.

Auer von Welsbach. By F. Sedlacek. 25 x 18 cm.; viii + 85 pp.; 30 illustrations. Berlin: Julius Springer, 1934. Price: 3.60 RM.

The present volume constitutes the second part of the larger book *Blätter für die Geschichte der Technik* edited by L. Erhard. The book opens with an interesting account of the parentage and family of Carl Auer von Welsbach from the early seventeenth century, and this is followed by an equally interesting account of his youth and studies. A brief survey of the development of the study of the rare earths leads to a description of the separation of the didymium of Mosander into the two elements praseodymium and neodymium by Auer. The three important contributions of Auer to the general amenities of the world, namely the incandescent gas mantle, the osmium lamp, and the cerium-iron alloys, used in the manufacture of automatic lighters, are considered at length in a manner which is intelligible to the non-scientific. The separation of the ytterbium of Marignac into aldebaranium and cassiopeium by Auer is described, and the whole question of his priority over Urbain is once more explored. The concluding chapter contains a fascinating account of the personality of Auer, who is here named the "Austrian Edison," his activities in the autumn of his life, and his death in 1929 at the age of 71.

This most interesting book is written in a very pleasant manner, and portraits of Auer at seven periods of his life are included. A list of references to the published works of Alois Auer von Welsbach, Carl Auer von Welsbach, and other writers on the subjects in which Auer was active is appended to the book.

The book is the story of a great Austrian, who was both a great man and a great chemist, his scientific investigations, and the development of some of these into vast industrial undertakings. It is a book well worth reading, and it can be recommended without reserve.

James F. Spence.

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Another new journal in the field of physical chemistry has made its appearance, and takes its place as an important scientific publication, access to which promises to be indispensable to those interested in mathematical, theoretical, or general physical chemistry, kinetics, catalysis, photochemistry, electrochemistry, and especially colloids and sorption,—the whole range of physical chemistry and chemical physics.

The board of editors consists of a dozen internationally known investigators. There are some forty permanent contributors distributed over seven cities of the U. S. S. R. The papers in Volume 1 are published in English, German, and occasionally French. Most of them are from the U. S. S. R., but a number are from other countries. Issues 3–4 contain the papers given at the Tenth Six-day Physico-Chemical Conference on Heterogeneous Catalysis, including one paper each from I. Langmuir and H. S. Taylor.

In a country which frankly recognizes scientific progress as a vital necessity and offers every inducement in its power for the pursuit of pure and applied science, it is inevitable that there should be enormous activity in every scientific field. The high quality of this journal in the selected field of physical chemistry commands our congratulations.

James W. McBain.

MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. V

SULFUR SOL

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A mechanism of the coagulation of sols by electrolytes based on adsorption and potentiometric measurements on hydrous oxide sols and arsenic trisulfide sol has been proposed in earlier papers (11, 13). While these papers were being prepared Bassett and Durrant (1) carried out experiments on Raffo's sulfur sol which indicated that the precipitating cation carried down by the coagulum was always exactly equivalent to the stabilizing polythionate ion originally held by the sulfur micelles. From this it was concluded that the coagulation is the result of a stoichiometric reaction between the soluble sodium salt of a sulfur polythionate complex and the precipitating electrolyte. Somewhat later Bolam and Bowden (2) and Bolam and Muir (4) determined the change in hydrogen-ion concentration on adding electrolytes to sulfur sol, using the same procedure as we employed with arsenic trisulfide sol. These observations led to the conclusion that the same fraction of hydrogen ion is liberated from the micelles of a given sulfur sol at the coagulation point, whatever the nature of the cation of the coagulating salt.

Since neither of the above conclusions reported by the English workers would be predicted from the mechanism of the coagulation process proposed by us, we have extended our observations on the nature of electrolyte coagulation to sulfur sols.

ADSORPTION EXPERIMENTS

Since the observations of Bassett and Durrant with the various cations were carried out on different sols, it was not possible to compare directly the amounts of the several cations taken up at the precipitation concentration. In order to make such a comparison the adsorption of a series of cations of varying valence was determined on samples of the same sol.

Preparation of sol

Raffo (8) sulfur sols were prepared according to the procedure of Bassett and Durrant: 83.6 g. of sodium thiosulfate crystals was dissolved in 50 cc.

of water and added to 65.5 cc. of concentrated sulfuric acid, keeping the temperature below 25°C. After adding 50 cc. of water, the mixture was heated to 85°C. until all sulfur dioxide was driven off. The mixture was allowed to stand at room temperature for three hours, the coagulated sulfur collected on a Buchner funnel, repeptized in cold water, and coagulated with 5 *N* sodium nitrate solution; the repeptization and coagulation were repeated three times. Since two or three liters of sol were required for each series of experiments, several portions were prepared and mixed after the first coagulation with sodium nitrate, subsequent coagulations and peptizations being carried out on the whole sol. After the second precipitation with sodium nitrate, the coagulated sulfur was peptized in a small amount of water and about one-fifth of this sol was used to wash the coagulum obtained by the next precipitation with sodium nitrate. In this way the amount of sodium nitrate retained by the sulfur was reduced. Four samples of sol of varying concentrations and ages were used in the following experiments:

TABLE 1

Adsorption by sulfur sol of cations at the precipitation concentration

NO. OF SOL	CC OF SOL	CATION ADDED	CATION CONCENTRATIONS MILLIEQ PER LITER		ADSORPTION MILLIEQ PER GRAM OF SULFUR
			Original	Final	
I. 5.4 g. per liter; age 50 days	150	Sr	5.87	2.00	0.73
	150	Ba	5.32	1.66	0.71
	150	Nd	3.68	0.20	0.68
II. 2.75 g. per liter; age 60 days	200	Ba	2.30	0.45	0.74
	175	Sr	3.07	1.30	0.72
	175	Ca	5.28	3.73	0.64
	400	Al	1.60	0.15	0.59
	400	Nd	1.34	0.08	0.52
	400	Th	1.39	0.38	0.41

Adsorption at the precipitation concentration

The precipitation concentration of electrolyte for the sulfur sol was taken as that concentration which was just sufficient to give a clear supernatant solution after the mixture of sol and electrolyte had stood for twenty-four hours. For each trial a 10-cc. portion of sol was employed. The electrolytes were the chlorides of the respective metals. The precipitation concentrations in milliequivalents per liter are given in the fourth column of table 1.

The adsorption measurements were made as follows: To a definite volume of sol contained in a wide-mouthed bottle, varying amounts of water and electrolyte were added to bring the mixture to some constant volume. The mixtures were stoppered, shaken, and allowed to stand for twenty-four hours. The coagulated sulfur was matted down by centrifuging, and the supernatant liquid filtered through a small filter paper to remove any suspended sulfur. The concentration of the cation in the filtrate was then determined. For standardization, samples in which water was substituted for the sol were subjected to the same treatment. Barium and strontium were determined as sulfates; the calcium was precipitated as oxalate and weighed as oxide; and the neodymium, aluminum, iron, and thorium were determined as oxides. All experiments were carried out in duplicate and the average is reported.

TABLE 2

Adsorption by sulfur sol of cations at concentrations above the precipitation values

NO OF SOL	CC OF SOL	CATION ADDED	CATION CONCENTRATIONS MILLIEQ. PER LITER		ADSORPTION MILLIEQ PER GRAM OF SULFUR
			Original	Final	
III. 7.3 g. per liter; age 5 days	50	Sr	10.12	6.12	0.56
	50	Al	7.73	3.31	0.66
	50	Nd	8.32	3.72	0.68
	50	Th	9.46	4.72	0.74
IV. 2.5 g. per liter; age 80 days	100	Ca	4.00	2.68	0.48
	100	Sr	4.00	2.42	0.58
	100	Ba	4.00	2.04	0.71
	100	Al	4.00	1.88	0.77
	100	Nd	4.00	0.82	1.16
	100	Th	4.00	0.68	1.21

The adsorption data at the precipitation values of the respective electrolytes are summarized in table 1.

Adsorption above the precipitation concentration

Observations similar to those described above were made (1) on a freshly formed sol with electrolyte concentrations approximately twice the respective precipitation values, and (2) on an aged sol with the respective electrolytes in equal concentrations well above the precipitation value. The results are summarized in table 2.

Discussion of results

Contrary to the belief of Bassett and Durrant, it is quite evident from the above results that the amounts of the several cations taken up by the particles of sulfur sol are not equivalent either at, or above, the respective precipitation concentrations. The order of precipitating power for sol I was found to be Nd > Ba > Sr, and the adsorption (at the precipitation value) in milliequivalents per gram of sulfur is in the order Sr > Ba > Nd. However, if we compare the relative amounts adsorbed we find that 94 per cent of the added neodymium is adsorbed as compared with 69 per cent of barium and 65 per cent of strontium.

In the case of sol II we find the order of precipitation to be Nd > Th > Al > Ba > Sr > Ca. The occurrence of the lyotropic sequence in the coagulation of sulfur sols has been pointed out by a number of investigators (12, 2, 5). The adsorption is in the order Ba > Sr > Ca > Al > Nd > Th. Again if we compare the percentage amounts of the added cations adsorbed, we find the order to be the same as that of the precipitating power, namely, Th > Nd > Al > Ba > Sr > Ca. As will be observed, tetravalent thorium does not precipitate in lower concentration than trivalent neodymium and the relative adsorption is less. Thorium chloride solution is hydrolyzed to a considerable degree, and we are dealing in this case with mutual coagulation of thorium oxide sol and sulfur sol as well as ionic interchange.

The order of adsorption well above the precipitation concentration, as shown in table 2, is the same as the order of precipitating power, namely, Th > Nd > Al > Ba > Sr > Ca. As will be shown in the subsequent experiments on hydrogen-ion displacement, cationic interchange is completed at or somewhat above the coagulation concentration. Further adsorption occurs, however, and may even lead to a reversal of charge and peptization in the case of thorium. The percentage adsorption from mixtures having the same electrolyte concentration is in the same order as the precipitating power. Thus in sol IV the relative amounts taken up are: thorium, 83 per cent; neodymium, 80 per cent; aluminum, 53 per cent; barium, 49 per cent; strontium, 40 per cent; and calcium, 33 per cent.

Similar observations were made on a Selmi (9) sol prepared by the interaction of hydrogen sulfide and sulfur dioxide (see page 1168); but the adsorption values with the more hydrophobic Selmi sol were smaller than with the Raffo sol.

Summarizing briefly, we note that the adsorption values of the precipitating ions are not equivalent at the precipitation concentration. The relatively more marked adsorption of the cations of higher valence brings about precipitation at lower concentrations.

TITRATION EXPERIMENTS

Preparation of sols

The displacement of hydrogen ion from the colloidal particles by the stepwise addition of various metallic chlorides was observed with both a

Raffo and a Selmi sol. The former was prepared by a method similar to that used by Bolam and Bowden: 25 cc. of concentrated sulfuric acid was added slowly from a dropping funnel to 100 cc. of saturated sodium thiosulfate. The mixture was stirred vigorously with a mechanical stirrer and the temperature was maintained between 20 and 25°C. by surrounding with ice water. After the reaction was complete the mixture was cooled to 0°C. and treated with 100 cc. of saturated sodium chloride solution. The coagulated sulfur was separated by centrifuging and heating to 85°C. with 100 cc. of water. Coagulation and repeptization were then repeated until the supernatant liquid after coagulation was neutral to litmus. Several portions having been prepared in this way, the whole was mixed and freed from sodium chloride by coagulating with concentrated hydrochloric acid and repeptizing by washing, the process being repeated several times. The sol was then dialyzed in a Neidle (7) dialyzer, using a cellophane bag, for three weeks at the rate of 500 cc. of water per hour. No chloride was detected in 100 cc. of dialysate evaporated to 10 cc. Sulfur which had settled out in the course of dialysis was removed by filtration. The sol contained 2.9 g. of sulfur per liter.

TABLE 3

Titration of a Raffo sulfur sol with alkali halides

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS $\times 10^4$	ΔE IN MILLIVOLTS	pH	$[H] \times 10^4$ IN SOLUTION	$[H] \times 10^4$ DISPLACED
None	0	53	3.08	8.3	0
KCl	38.4	59	2.98	10.5	2.2
	76.8	60.5	2.96	11.0	2.7
	115.2	61.0	2.95	11.2	2.9
	153.6	64.0	2.90	12.6	4.3
	192.0	65.5	2.87	13.5	5.2
NaCl	38.4	57.5	3.00	10.0	1.7
	76.8	61.0	2.95	11.2	2.9
	115.2	62.5	2.92	12.0	3.7
	153.6	63.5	2.91	12.3	4.0
	192.0	64.5	2.89	12.9	4.6
LiCl	38.4	57.0	3.01	9.8	1.5
	76.8	60.0	2.96	11.0	2.7
	115.2	61.5	2.94	11.5	3.2
	153.6	62.5	2.92	12.0	3.7
	192.0	63.5	2.91	12.3	4.0

The Selmi sol was prepared by the method of Weiser and Cunningham (12, 2, 5). Hydrogen sulfide and sulfur dioxide were passed simultaneously into water previously saturated with sulfur dioxide. Hydrogen was used to wash out the excess gases. After standing thirty days, the sol was filtered and the titration experiments carried out. The sol contained 10.8 g. of sulfur per liter.

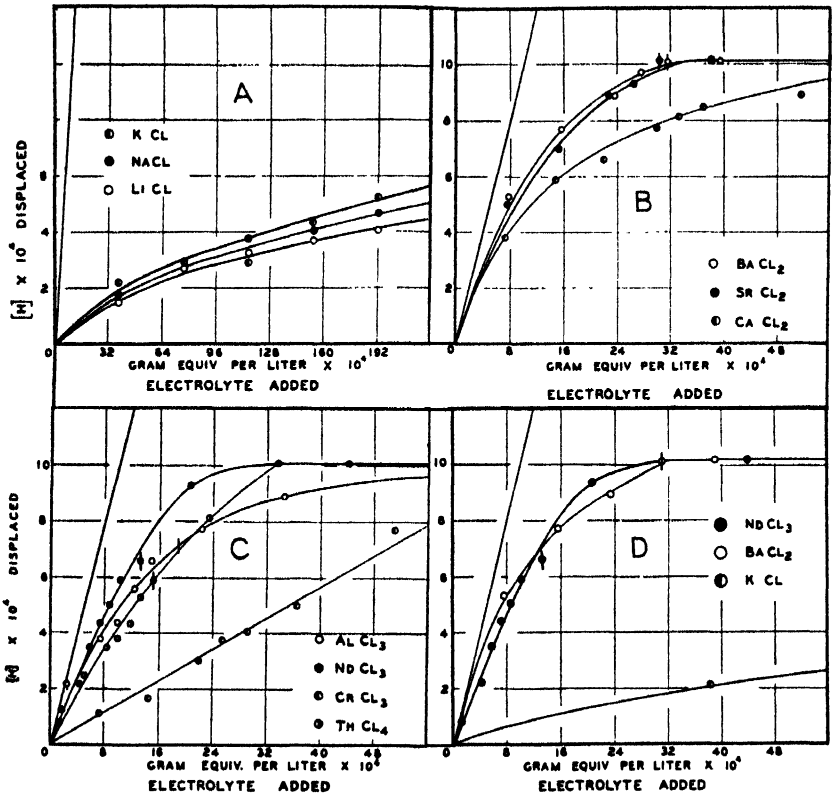

FIG. 1. TITRATION OF RAFFO SOL WITH ELECTROLYTES

Potentiometric titrations on the Raffo sol

To 5-cc. portions of sol contained in small weighing bottles were added varying amounts of water and precipitating electrolyte, bringing the final volume in each case to 5.1 cc. A microburet graduated in 0.01 cc. was used to deliver the water and solutions. After thorough mixing the samples were allowed to stand in a thermostat for eighteen hours before making the potentiometric measurements.

The glass electrode used to determine the pH value was of the MacInnes and Dole type (6). A bulb was blown on the end of a glass tube (Corning No. 015) until the resulting film was thin enough to show interference colors. The end of a tube of the same glass, one-half inch in diameter, was heated to low red heat and placed against the bulb. The adhering film was fused on by careful heating. The tube, except for the lower one-half inch, was covered with paraffin. After the tube had soaked for two days in 0.01 *N* hydrochloric acid, it was rinsed and filled almost to the level of the paraffin with 0.01 *N* hydrochloric acid saturated with quinhydrone, thus forming a quinhydrone half-cell. This electrode was suspended in the weighing bottle containing the sol–electrolyte mixture. The other half-cell was a 0.01 *N* calomel electrode, the tip of the salt bridge making contact with the liquid in the weighing bottle. Such dilute potassium chloride shows no coagulating action on the sol. The Youden glass electrode hydrogen-ion apparatus manufactured by the W. M. Welch Company was employed in measuring the E.M.F. The null-point instrument used in this apparatus is the Lindemann electrometer.

TABLE 4

Titration of a Raffo sulfur sol with alkaline earth halides

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS × 10^4	*E* IN MILLIVOLTS	pH	[H] × 10^4 IN SOLUTION	[H] × 10^4 DISPLACED
None ...	0	53.5	3.07	8.5	0
$BaCl_2$	7.88	66.0	2.86	13.8	5.3
	15.76	70.0	2.79	16.2	7.7
	23.64	72.0	2.76	17.4	8.9
	27.58	73.0	2.74	18.2	9.7
	31.52	74.0	2.73	18.6	10.1
	39.4	74.0	2.73	18.6	10.1
$SrCl_2$	7.60	65.5	2.87	13.5	5.0
	15.20	69.0	2.81	15.5	7.0
	22.80	72.0	2.76	17.4	8.9
	26.60	72.5	2.75	17.8	9.3
	30.40	74.0	2.73	18.6	10.1
	38.0	73.5	2.73	18.6	10.1
$CaCl_2$	7.38	63.0	2.91	12.3	3.8
	14.76	67.0	2.84	14.4	5.9
	22.14	68.5	2.82	15.1	6.6
	29.52	70.0	2.79	16.2	7.7
	33.21	70.5	2.78	16.6	8.1
	36.90	71.5	2.77	17.0	8.5
	51.66	72.0	2.76	17.4	8.9

The glass electrode was standardized with *M*/20 potassium acid phthalate. Other standard buffers of lower pH were frequently run as controls.

The sol was titrated with the chlorides of potassium, sodium, lithium, barium, strontium, calcium, neodymium, aluminum, chromium, and thorium. The data for the alkali chlorides are recorded in table 3 and shown graphically in figure 1A. Since a relatively high concentration of

TABLE 5

Titration of a Raffo sol with $NdCl_3$, $AlCl_3$, $CrCl_3$, *and* $ThCl_4$

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS × 10^4	*E* IN MILLIVOLTS	pH	[H] × 10^4 IN SOLUTION	[H] × 10^4 DISPLACED
None	0	53.5	3.07	8.5	0
$NdCl_3$	1.47	56.0	3.03	9.3	0.8
	4.41	59.5	2.97	10.7	2.2
	5.88	62.5	2.92	12.0	3.5
	7.35	64.5	2.89	12.9	4.4
	8.82	65.5	2.87	13.5	5.0
	10.29	67.0	2.84	14.4	5.9
	13.23	68.5	2.85	15.1	6.6
	20.58	72.5	2.75	17.8	9.3
	44.10	74.0	2.73	18.6	10.1
$AlCl_3$	2.48	59.5	2.97	10.7	2.2
	7.44	63.5	2.91	12.3	3.8
	9.92	64.5	2.89	12.9	4.4
	12.40	66.5	2.85	14.1	5.6
	14.88	68.5	2.82	15.1	6.6
	22.32	70.5	2.79	16.2	7.7
	34.72	72.0	2.76	17.4	8.9
$CrCl_3$	7.32	56.5	3.02	9.6	1.1
	14.64	58.5	2.99	10.2	1.7
	21.96	61.5	2.94	11.5	3.0
	25.62	63.0	2.91	12.3	3.8
	29.28	64.0	2.90	12.6	4.1
	36.60	65.5	2.87	13.5	5.0
	51.24	70.0	2.79	16.2	7.7
$ThCl_4$	1.68	57.5	3.01	9.8	1.3
	5.04	60.0	2.96	11.0	2.5
	8.40	62.5	2.92	12.0	3.5
	10.08	63.5	2.91	12.3	3.8
	11.76	64.5	2.89	12.9	4.4
	13.44	66.0	2.86	13.8	5.3
	15.12	67.5	2.84	14.4	5.9
	23.52	71.0	2.78	16.6	8.1
	33.60	74.0	2.73	18.6	10.1

the alkali cations is necessary to cause coagulation, the titrations were not carried to the precipitation value on account of the possibility of serious error in the pH measurements at the higher concentrations.

The results of the titration of the sol with the alkaline earth halides are given in table 4 and shown graphically in figure 1B. The precipitation concentration is indicated by a short vertical line cutting the curve for hydrogen displacement.

The titration data for the cations of higher valence are shown in table 5 and figure 1C.

Referring to figure 1A it will be seen that the displacement curves for the monovalent ions are similar in form. The hydrogen ion displaced is markedly less than equivalent to the cation added (straight line). The displacing power of the cations is in the same order as their precipitating power: K > Na > Li. A similar lyotropic sequence is observed in the case of the divalent ions (figure 1B). Although the displacing powers of barium and strontium are almost the same as are the precipitation values, that of calcium is distinctly lower. Comparing the displacement curves with the straight line representing the cation added, it will be noted that at low concentrations about 60 per cent of the cation added is effective in displacing hydrogen ion, the effectiveness falling off with increasing concentration until the coagulation value is reached, above which no further displacement occurs. With the cations of higher valence, figure 1C, the order of displacing power and coagulating power is the same: Nd > Th > Al > Cr. The reason thorium is less effective than neodymium has been discussed in connection with the adsorption experiments. In contrast to the behavior of the alkaline earth cations, thorium, neodymium, and aluminum coagulate the sol before the maximum displacement of hydrogen ion is attained, indicating further ionic interchange after the charge on the particles has been reduced to the point of coagulation.

Contrary to the view of Bolam and Muir, the displacement of hydrogen ion is not the same at the coagulation point. This is emphasized in figure 1D, which shows that much less hydrogen is displaced at the precipitation value of neodymium than at the precipitation value of barium. Less neodymium ion needs to be adsorbed to lower the charge to the critical coagulation value and accordingly less hydrogen is displaced at the precipitation value of neodymium than of barium.

Potentiometric titrations on the Selmi sol

Observations were made on the more hydrophobic Selmi sol similar to those on the Raffo sol. To conserve space the tables of titration data are omitted, the results being shown graphically in figure 2.

The displacement curves with the monovalent ions, figure 2A, are the same in form as those obtained with the Raffo sol. With the divalent ions the order of displacing power and coagulating power is: Ba > Sr > Ca. The difference in displacing power is slight at lower concentrations, becoming more marked as the precipitation concentration is approached. With the ions of higher valence the curves are quite similar in form, the order of displacing power being: Th > Nd > Cr > Al. This is the same as the order of precipitating power, with the exception that the chlorides of chromium and aluminum precipitate in almost the same concentration. It will be noted that at low concentrations of thorium and neodymium the hydrogen ion displaced is almost equivalent to the cation added (straight line). As in the case of the Raffo sol, the displacement of hydrogen ion is far from complete at the precipitation concentration of the strongly adsorbed multivalent ions. For these ions which precipitate in low concentrations that are not far apart, the displacement of hydrogen at the precipitation value of the several ions approaches equivalence in accord with the observations of Bolam and Muir. On the other hand, with ions whose precipitation values are not close together, such as barium and neodymium, the displacement of hydrogen at the precipitation value of the former is much greater than at the precipitation value of the latter

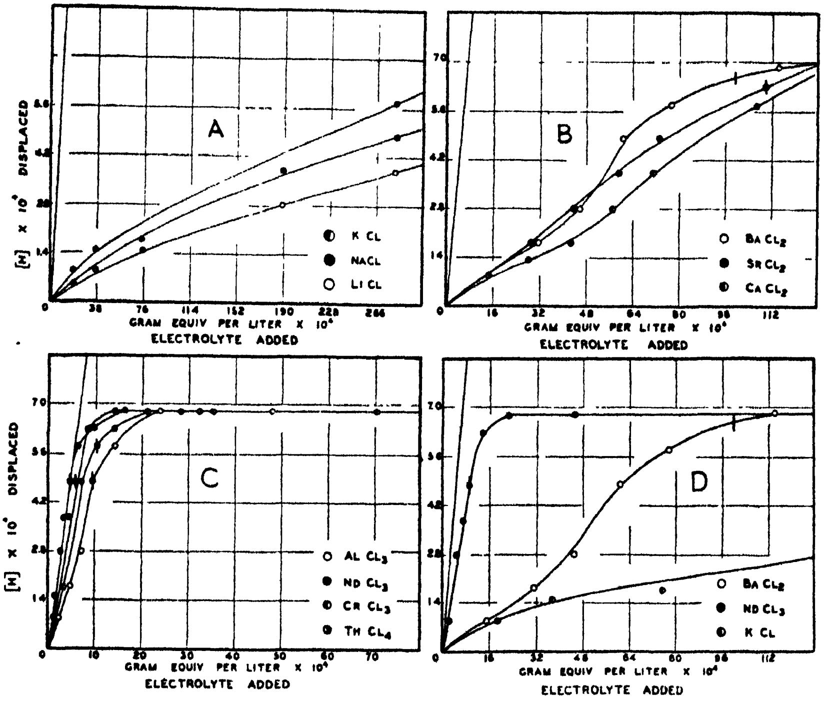

FIG. 2. TITRATION OF SELMI SOL WITH ELECTROLYTES

(cf. figure 2B), just as was found in the case of the Raffo sol, and for the same reason.

Comparing the observations on the two sols we find the hydrogen-ion concentration of the original Selmi sol to be over four times that of the Raffo sol, whereas after coagulation the ratio in the supernatant solution was reduced to 5:2. Moreover, the effect of the valence of the cation is more marked in the aged Selmi sol than in the Raffo sol. The aging of the former causes it to assume the properties of a typical hydrophobic sol in which the valence and lyotropic influence of the cations is more marked than in the more hydrophilic Raffo sol.

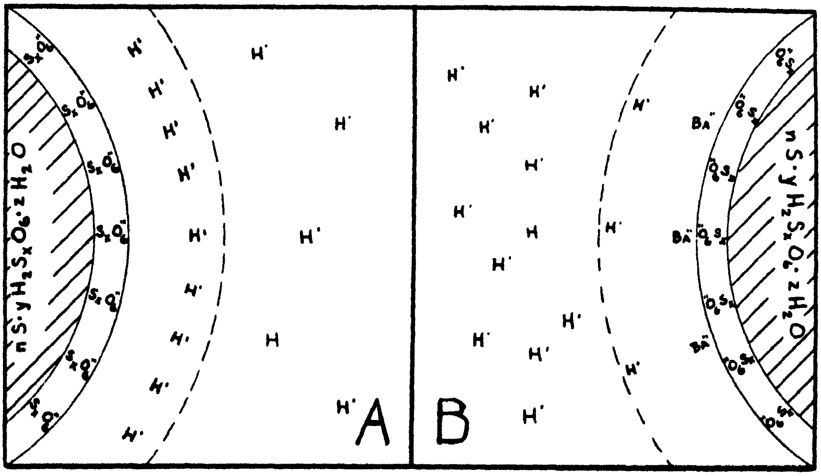

FIG. 3. DIAGRAMMATIC REPRESENTATION OF THE CONSTITUTION OF A PARTICLE OF COLLOIDAL SULFUR BEFORE AND AFTER THE ADDITION OF BARIUM CHLORIDE

MECHANISM OF THE COAGULATION

In sulfur sols prepared by the decomposition of sulfur compounds, the stabilizing electrolytes are polythionic acids, such as pentathionic and hexathionic, which may be represented by the general formula $H_2S_xO_6$. The colloidal particles consist essentially of a nucleus of colloidal sulfur which adsorbs the polythionate ions so strongly that the latter constitute the inner portion of the double layer surrounding the particles and give the particles a negative charge. The outer layer is a diffuse layer of hydrogen ions. The constitution may be represented diagrammatically as shown in figure 3A. The hydrogen ions of the outer layer are osmotically active and have a range of movement determined by the electrostatic field due to the residual $S_xO_6^{--}$ on the surface. Some of the hydrogen ions, shown beyond the dotted line, have sufficient osmotic pressure so that they can be measured potentiometrically. Others are so firmly held by the $S_xO_6^{--}$ layer that they do not influence the hydrogen electrode.

On the addition of an electrolyte, an exchange takes place between some of the hydrogen ions held by the $S_xO_6^{--}$ and the cations in the external liquid. The theory of the diffuse double layer indicates that coagulation occurs when the potential on the particles has fallen below a critical value, as a consequence of the contraction of the double layer by the coagulating ion. The more strongly adsorbed metal ions displace hydrogen ions and take up a position relatively closer to the inner layer, as indicated with barium ion in figure 3B. Monovalent cations are weakly adsorbed and bring about a much smaller displacement of hydrogen ions than an equivalent amount of multivalent ions. Trivalent cations are more effective than divalent, for example, less Nd^{+++} than Ba^{++} needs to be adsorbed to reduce the potential to the coagulation point, and precipitation takes place with lower concentration of neodymium salts than with barium salts. Since less neodymium than barium needs to be adsorbed to reduce the potential to the coagulation point, less hydrogen is displaced from the outer layer at the precipitation value of neodymium than of barium ion. The displacement of hydrogen by cations at the precipitation value approaches equivalence only in case the respective precipitation values are relatively close together.

For cations of the same valence, a definite sequence is shown in the flocculating power; thus the order is K > Na > Li, and Ba > Sr > Ca. Voet and Balkema (10) showed that when different ions of the same valence have the same concentration in the medium, the smaller ions have the smaller concentration in the double layer. As the magnitude of the contraction of the double layer depends on the concentration of the cations, it is evident that the larger ions have the greater effect and show therefore the greater decrease in the electrokinetic potential and the greater flocculating power.

SUMMARY

The following is a brief summary of the results of this investigation:

1. The adsorption of thorium, neodymium, aluminum, barium, strontium, and calcium during the coagulation of Raffo sulfur sols has been determined at the coagulation concentration and at higher concentrations. Contrary to the results of Bassett and Durrant, the adsorption values of the various cations are not equivalent at the respective precipitation concentrations.

2. At the precipitation concentration, the order of adsorption of the several cations expressed in milliequivalents per gram of sulfur is in inverse order to the precipitating power. However, if one compares the fraction of the precipitation value adsorbed, the adsorption is in the same order as the coagulating power.

3. The order of adsorption above the precipitation value is the same as that of the precipitating power: Th > Nd > Al > Ba > Sr > Ca.

4. The displacement of hydrogen ions during the stepwise addition of electrolytes to both Raffo and Selmi sols has been followed potentiometrically, using the glass electrode.

5. The hydrogen-ion displacement by the several cations is in the same order as the coagulating power.

6. Equivalent amounts of hydrogen ion are not displaced at the precipitation value of the several cations, as claimed by Bolam and Muir. The displacement approaches equivalence only when the precipitation values are of the same order of magnitude.

7. With cations of the same valence, the order of hydrogen-ion displacement as well as coagulating power is related to the size of the ions. At the same concentration, the largest ion produces the greatest displacement. Thus we find the order to be as follows: K > Na > Li, and Ba > Sr > Ca.

8. A mechanism has been proposed to account for the above-mentioned phenomena of adsorption and displacement of hydrogen ion which accompany the processes of potential reduction and coagulation.

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A STUDY OF THE DILATOMETRIC METHOD FOR FOLLOWING THE HYDROLYSIS OF SUCROSE

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INTRODUCTION

Dilatometers have been successfully used by Åkerlöf (1) and Brönsted (4), among others, in precise studies of the kinetics of catalyzed reactions. More recently, dilatometers have been applied by Sreenivasaya (15) and Rona (14) to the study of the hydrolysis of sucrose in the presence of invertase. These workers reported that the change in volume was proportional to the change in rotation, and that the total contraction accompanying the hydrolysis varied only with the amount of sucrose present, being 6 cc. per mole.

The figures averaged by Rona (14) to obtain this value showed considerable scattering, and were not obtained by direct observation of the total volume change from the beginning to end of the hydrolysis, but by calculation from the known changes in rotation and the proportionality between changes in volume and in rotation. Sreenivasaya (15) stated that he had confirmed Rona's figure by direct observation in a special dilatometer in which the reaction could be started as well as finished, but he gave no detailed data for his experiments with invertase. Since Riiber (13) had found that the mutarotation of glucose and fructose was accompanied by a small increase in volume, it seemed unlikely that the kinetics of the volume change could be exactly the same as that of the hydrolysis itself. This effect of mutarotation is avoided in the best polarimetric technique by the addition of alkali before the rotation is measured, but it does not seem possible to avoid it in a dilatometer. Yet, if the dilatometric method could be shown to be reliable, it would make possible the study of this important enzyme in a laboratory not provided with an expensive polarimeter.

The object of the present work, therefore, was to find out how well the dilatometric method would reproduce the known characteristics of invertase action, as well as those of the hydrolysis of sucrose under the influence of hydrochloric acid.

EXPERIMENTAL

Materials

Invertase was prepared from baker's yeast by the method of Nelson and Born (10), with the omission of the precipitations by alcohol and the treatment with kaolin. A very similar method has been included in those of the Association of Official Agricultural Chemists (2). The solution was dialyzed to a specific conductivity of about 10^{-5}. Its solid content was 0.95 per cent, and the dry matter contained 1.56 per cent of nitrogen. This solution was diluted to one-tenth of the above concentration with distilled water, and the invertase concentrations mentioned below refer to cubic centimeters of this diluted solution in 100 cc. of the reacting mixture.

The sucrose used was granulated table sugar, of a brand sold in sealed cartons. Its ash and moisture contents were found to be negligible, 0.0075 and 0.02 per cent, respectively. It was not further purified because one of us had previously found the specific rotation of other samples of the same brand to agree with the accepted value within 0.1 per cent.

The acidity of the sucrose–invertase solutions was regulated by acetate buffers prepared from standardized solutions of C.P. acetic acid and sodium hydroxide. The concentration of both acid and salt in each reaction mixture was 0.01 *M*. The acidity of the reaction mixtures was measured electrometrically at 25°C., using hydrogen electrodes with a saturated potassium chloride junction. The pH values are based on 0.1 *M* hydrochloric acid as standard, its pH being taken as 1.075. Hydrochloric acid solutions were prepared by diluting weighed amounts of the constant-boiling mixture, the concentrations being checked by weighing silver chloride.

Apparatus and method

The dilatometers were constructed of Pyrex glass and were like that depicted by Åkerlöf (1), without a water jacket around the capillary tube.[1] Two instruments were used, of such dimensions that the total change observed was always between 10 and 50 cm., in most cases about 25 cm. The larger dilatometer had a capacity of 182.6 cc., and a fall of 1 cm. in its tube corresponded to a contraction of 2.56 cu. mm. The corresponding figures for the smaller dilatometer were 92.8 cc. and 3.67 cu. mm. per centimeter. The height of the meniscus in the capillary was read to 0.01 cm. by means of a scale of millimeter paper and a hand lens. The temperature of the dilatometers was controlled by a well-stirred bath containing about 300 l. of water, maintained at 25° ± 0.003°C. During some of the experiments which were done in hot weather, it was necessary to cool the surface of the bath by an electric fan, but the regulation was just as good as in cooler weather. Each dilatometer was supported in a brass rack and immersed to a level a few millimeters above the base of the capillary tube.

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[1] The writers are indebted to Dr. G. Åkerlöf for several pieces of selected capillary tubing.

Before each experiment the dilatometer was cleaned with chromic acid solution, washed with water and alcohol, and dried by a current of air. It was then kept in the bath at least fifteen minutes before being filled. In filling the dilatometer, solution was transferred from an Erlenmeyer flask in the bath through a delivery tube connected by a short piece of rubber tubing to the side arm of the dilatometer. The solution was driven over by air pressure applied above the surface of the liquid in the flask. Air bubbles were removed by alternately applying and releasing the pressure during the filling. When the meniscus had risen to the desired part of the capillary, the stopcock was tightly closed and readings were begun, without the introduction of a mercury column. Control experiments with water, or sugar solution without a catalyst, showed constancy of level only after eight or ten minutes, because of temperature changes during the passage of the solution through the delivery tube and side arm, which were not immersed in the bath. After this initial period the level in the control experiments remained constant within 0.02 cm. for many days, proving the absence of leakage and the adequacy of the temperature control.

In the enzyme experiments, the reaction was started by adding invertase solution from a volumetric pipet to a measured volume of buffered sugar solution. Each pipet was calibrated at 25°C., after part of its tip had been cut off to allow it to deliver completely within five to ten seconds. Complete mixing was assured by shaking within ten seconds of the start, which was taken as the time when half of the enzyme solution had left the pipet. Experiments with 0.1 *M* hydrochloric acid as catalyst were started in the same way. In the case of the more concentrated acid solutions, equal volumes of double strength acid and sugar solutions were brought to 25°C. in separate flasks, and mixed by pouring rapidly from one flask into the other and back again. Titrations of the acid solutions showed that when 2.0 *M* hydrochloric acid was mixed in this way with an equal volume of 20 per cent sugar, the acid concentration of the resulting solution was only 0.25 per cent greater than 1.0 *M*. In reporting the results, this slight deviation from simple proportionality on dilution has been neglected.

Final readings, after the completion of the hydrolysis, were constant (± 0.01 cm.) after one to three days in the invertase experiments. With 0.1 *M* hydrochloric acid, the level was constant from the sixth or seventh to at least the tenth or twelfth day. With 0.5 *M* acid, the level remained constant during the second day, but in some cases rose gradually after that. With 1.0 *M* acid, the level always passed through a minimum and then rose gradually, the minimum occurring after about ten hours with 10 per cent sugar and after about twenty-four hours with the more dilute solutions. Since this slow increase in volume was presumably due to some secondary action of the strong acid on invert sugar, the lowest observed value was taken as the final reading with respect to the hydrolysis.

Calculation of reaction velocities

Since the method used in these experiments does not give directly a value for the initial reading at the time of starting the reaction, the attempt was made to express the reaction velocity in such a way as to avoid the use of an initial reading. This could easily be done in the case of the experiments with acid, because it was found that the volume change followed .the unimolecular law. The unimolecular velocity constant was calculated by the short interval formula,

$$k = \frac{1}{t_2 - t_1} \log \frac{R_1 - R_\infty}{R_2 - R_\infty} \tag{1}$$

where t is time in minutes and R is the corresponding reading of the dilatometer, in centimeters measured upwards along the capillary from an arbitrary zero point. The velocity constants so calculated, from points corresponding to five or six equally spaced readings of volume, were fully as constant as those recorded by others in polarimetric experiments, and the average of four or five such values was taken as the best measure of the reaction velocity in each experiment. To obtain a value for the total volume change corresponding to complete hydrolysis, the average value of k from equation 1 was put into the unimolecular equation in the long interval form,

$$k = \frac{1}{t} \log \frac{R_0 - R_\infty}{R - R_\infty} \tag{2}$$

which was solved for $R_0 - R_\infty$, the distance in centimeters corresponding to the total volume change. For comparison with the invertase experiments, the velocities were also expressed in terms of the half period, $t_{0.5}$, which is the time in minutes required for one-half of the total change in volume. These values were likewise obtained from the average values of k from equation 1, by the use of equation 2 in the form,

$$t_{0.5} = \frac{1}{k} \log 2 = \frac{0.3010}{k} \tag{3}$$

In the case of the invertase experiments the problem was more difficult, because the course of the reaction does not follow any theoretical velocity equation. If the dilatometer readings are plotted against time, the curve obtained is concave upwards, the volume decreasing less and less rapidly as the reaction proceeds. During the first 10 or 20 per cent of the change the curve is practically a straight line, just as in polarimetric experiments. With the polarimeter, these linear initial velocities can be used as a reliable measure of the reaction velocity (7, 8, 9). With this dilatometric method, the points obtained during the first ten minutes could not be used. However, when the readings obtained after ten minutes were plotted against time on a large scale, they appeared to fall on straight lines for a considerable further interval. These lines were extrapolated back to zero time to give an initial reading, which was recorded as a minimum value, since, if the line is not really straight, it must be concave upwards.

When the logarithms of the experimental values of $R - R_\infty$ were plotted against time, curves were obtained which were concave downwards, at least up to about 90 per cent completion. This is an indication of the established fact that the unimolecular velocity coefficient increases with time in invertase experiments (8, 12). The curves could be extrapolated back to zero time by the use of a flexible spline, giving values of log $(R_0 - R_\infty)$. These values are likely to be too high, because in extrapolating a curve the tendency is to approach a straight line rather than to increase the curvature. Hence the two methods of extrapolation should give a minimum and a maximum value, respectively, for the total volume change in each experiment. These extrapolations were made from large scale plots of the data obtained in all of the invertase experiments, and the semi-logarithmic plot did, in fact, give somewhat higher values for the total change than the direct plot in twenty out of twenty-three cases. Since the two sets of values did not differ by more than 1.1 per cent in the extreme case, and their average difference was less than 0.5 per cent, it was considered that the average of the two extrapolated values would give a reliable value for the total volume change in each experiment.

These average values for the total change were used to obtain the half-period from the large scale semi-logarithmic plots. It was considered that the reciprocal of the half-period was a better measure of the reaction velocity than the apparent initial slope of the direct plot, since in obtaining the latter there was always uncertainty as to whether the points used were really on the straight part of the curve.

The half-period may be translated into a unimolecular velocity coefficient by the use of equation 3, but such coefficients are without theoretical significance in the case of invertase experiments because the reaction does not follow the unimolecular law.

RESULTS AND DISCUSSION

The results of the principal experiments are summarized in tables 1 and 2. Each figure is the mean of those obtained from concordant duplicate experiments.

Hydrolysis by acid

The data of table 1 indicate that for each concentration of sucrose the velocity constant increases with the acid concentration, but that the increase is more than proportional. This variation is exhibited in figure 1, in which the ratios of velocity constant to acid concentration are plotted as functions of the acid concentration. Each curve is marked with the initial sucrose concentration in grams per 100 cc. The points indicated as half-inked circles represent the polarimetric data of Lamble and Lewis (6) for 10 per cent sucrose solutions at 25°C. The agreement of their data with ours is a satisfactory indication that the two methods measure the velocity of the same reaction.

TABLE 1

Rate and extent of contraction in volume of sucrose-hydrochloric acid solutions at 25°C.

SUCROSE PER 100 CC. OF SOLUTION	HCl PER LITER OF SOLUTION	VELOCITY CONSTANT (BASE 10) × 1000	HALF-PERIOD	TOTAL CONTRACTION PER MOLE OF SUCROSE
grams	*moles*	*1000/minutes*	*minutes*	*cc.*
2	0.0972	0 325	926	6 77
2	0.486	1.95	154.4	6 63
2	0.972	4 95	60 8	6 44
5	0.0953	0.330	912	6.62
5	0.486	2.04	147.5	6.45
5	0.972	5.15	58.4	6 25
10*	0.0952	0.343	877	6.49
10	0.486	2.15	139.8	6 31
10	0 952	5.26	57 2	6.14

* Not done in duplicate.

TABLE 2

Rate and extent of contraction in volume of sucrose–invertase solutions at 25°C.

SUCROSE PER 100 CC. OF SOLUTION	INVERTASE PER 100 CC OF SOLUTION	ACIDITY	HALF-PERIOD	TOTAL CONTRACTION PER MOLE OF SUCROSE
grams	*cc. of stock solution*	pH	*minutes*	*cc.*
2	0.4	4.67–4.70	344	6.82
2	1.0	4.67–4.70	138.7	6.85
2	2.0	4.67–4.70	68.7	6.91
5	1.0	4.67–4.70	296	6.67
5	2.5	4 67–4.70	117.1	6.70
5	5.0	4.67–4.70	58.5	6.76
10	2.0	4.67–4.70	316	6.52
10	5.0	4.67–4.70	125.2	6.58
10	10.0	4.67–4.70	62.8	6.59

Figure 2 shows the constancy of the unimolecular velocity coefficient throughout the course of the volume change in individual experiments. The abscissas represent the percentage of the total contraction occurring in the time t, and the ordinates are the values of 1000 k, calculated from the unimolecular law, equation 2. It is evident from figure 2 that there is no trend in the successive values of k, and that they are constant within 0.5 per cent or better.

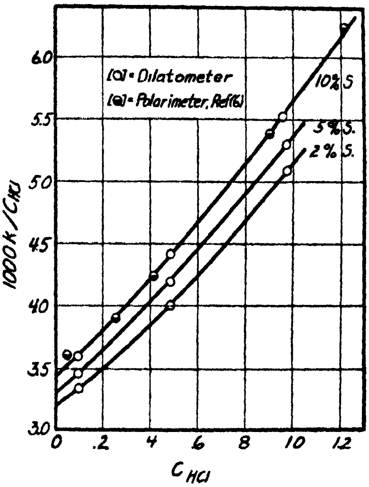

FIG. 1. EFFECT OF ACID CONCENTRATION ON THE RATE OF CONTRACTION OF SUCROSE–HYDROCHLORIC ACID SOLUTIONS

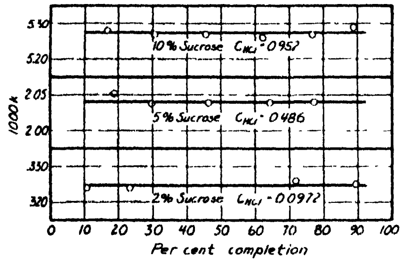

FIG. 2

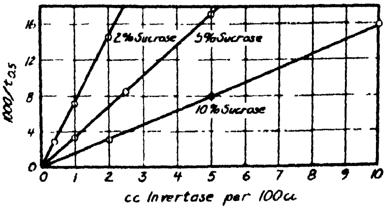

FIG. 3

FIG. 2. APPLICABILITY OF THE UNIMOLECULAR LAW TO THE KINETICS OF THE CONTRACTION OF SUCROSE–HYDROCHLORIC ACID SOLUTIONS

FIG. 3. EFFECT OF INVERTASE CONCENTRATION ON THE RATE OF CONTRACTION OF SUCROSE–INVERTASE SOLUTIONS

Hydrolysis by invertase

When the hydrolysis of sucrose is catalyzed by invertase, it has been found in polarimetric experiments that the reaction velocity is closely proportional to the concentration of the enzyme (7, 12, 11). The data in table 1 and figure 3 show that this simple relation is also true for the rate of the volume change, if the rate is taken as proportional to the reciprocal of the half-period. Such exact proportionality could not be obtained, however, by using the apparent initial slopes as a measure of the reaction velocity. On this basis the velocity of the faster reactions appeared to fall below the line of proportionality, which indicates that the slopes used were too small.

The effect of the initial sucrose concentration on the velocity of hydrolysis by invertase has usually been expressed by plotting the actual velocity, in degrees of change in rotation or amount of sucrose hydrolyzed in unit time, against the initial concentration. The curves so obtained show that the velocity at first increases rapidly with the concentration, but reaches a rather flat maximum at concentrations of about 5 to 10 g. of sucrose per 100 cc. (8, 12, 9). The data for each experiment in table 2 were translated into similar units by dividing the initial sucrose concentration by the product of the half-period and the invertase concentration, and then reduced to relative velocities by dividing by the maximum velocity. The effect of the initial sucrose concentration on the relative velocity is shown in figure 4, in which the full circles represent the dilatometric data and the half-inked circles represent the polarimetric experiments of Nelson and coworkers[2] (12, 9). Except for the point for 10 per cent sucrose, the dilatometric data agree with the polarimetric fully as well as the two sets of polarimetric data agree with each other.

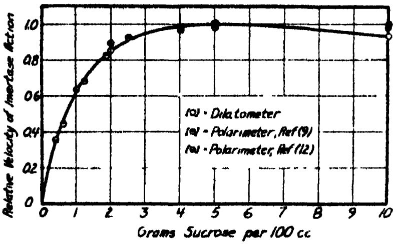

FIG. 4

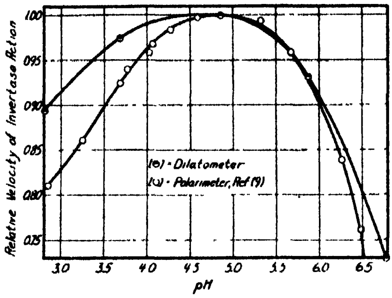

FIG. 5

FIG. 4. EFFECT OF INITIAL SUCROSE CONCENTRATION ON THE RELATIVE RATE OF CONTRACTION OF SUCROSE-INVERTASE SOLUTIONS

FIG. 5. EFFECT OF pH ON THE RELATIVE RATE OF CONTRACTION OF SUCROSE-INVERTASE SOLUTIONS

The effect of pH on the velocity of the volume change during the hydrolysis by invertase was studied by additional experiments not shown in table 2. The pH was varied by the use of buffers of secondary sodium citrate and hydrochloric acid or sodium hydroxide, the total citrate concentration being 0.01 *M* in each reaction mixture. The sucrose concentration was 5 g. per 100 cc., and the invertase concentration was 5 cc. per 100 cc. The reaction velocities were expressed as reciprocals of the half-period, and reduced to relative velocities by dividing by the maximum velocity. Figure 5 shows the effect of pH on the relative velocity. Here the half-inked circles represent the dilatometric data, while the full circles represent polarimetric data of Nelson and Bloomfield (9). The two methods give the same optimum zone of pH values, about 4.5 to 5.0, but the velocities of the volume change appear to fall off less sharply with changes in acidity than those obtained by the polarimeter. This may be a real difference in the results of the two methods, or it may conceivably be due to peculiarities of the different invertase preparations. It is not due to the fact that Nelson and Bloomfield's experiments were done with 10 per cent sucrose solutions, for an additional set of dilatometric experiments with this concentration gave results very similar to those shown for the 5 per cent solutions.[3]

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[2] In Nelson and Bloomfield's table 1 (ref. 9, p. 1027), the third figure in the fourth column should be 0.985 instead of 0.085. In Nelson and Vosburgh's table 5 (ref. 12, p. 803), the last figure in the last column should be 0.0118 instead of 0.0085.

The kinetics of the volume change in the individual experiments were found to be like that of the chemical change, as determined by the polarimeter, in that the unimolecular velocity coefficients increased with time throughout the greater part of the reaction. It was possible also to reproduce with the dilatometer the peculiarity recently described by White (16), who found in polarimetric experiments with invertase that the unimolecular velocity coefficient passed through a maximum and decreased after the reaction was 90 to 96 per cent complete.

Several equations which have been proposed by various workers (5, 8, 11, 3, 16) to represent the kinetics of invertase action were applied to the dilatometric data, but none of them was found to give an accurate description of the whole course of the volume change. This was not surprising, for even if an equation did represent the true course of the hydrolysis, it would probably not fit the course of the volume change, because the latter includes the effect of mutarotation.

Variations in the total volume change

One unexpected result of the present investigation was that the total decrease in volume during the hydrolysis of a given amount of sucrose appeared to vary with the concentration of the catalyst. Moreover, the total volume change was not exactly proportional to the initial sucrose concentration. This is contrary to the conclusions of previous workers (15, 14). The last columns in tables 1 and 2 give the extent of the total decrease in volume observed from the beginning to the end of each reaction, expressed as cubic centimeters per mole of sucrose initially present. These data are plotted against the concentrations of catalyst in figure 6. It will be observed that the total change is practically a linear function of the concentration of the catalyst, and that it increases with the concentration of invertase, but decreases with the concentration of hydrochloric acid. This decrease may possibly be connected with the onset of the secondary reaction, which was inferred from the slow ultimate increase in volume observed in the experiments with 0.5 and 1.0 M acid. No explanation has been found for the less marked increase in the total change observed as the concentration of invertase was increased. The constancy of the end point in these experiments left nothing to be desired, and the extrapolated values for the initial readings are believed to be reliable, for the reasons already given. In polarimetric experiments, it has always been found that the total change in rotation is independent of the invertase concentration, and it is generally believed that the hydrolysis always proceeds to completion.

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[3] Professor J. M. Nelson (private communication) writes that the difference between the two curves of figure 5 in the more acid region is to be expected, since Dr. E. L. Saul, working at Columbia University, has been able to vary this branch of the curve at will by dilution of certain invertase solutions or by adding extraneous material.

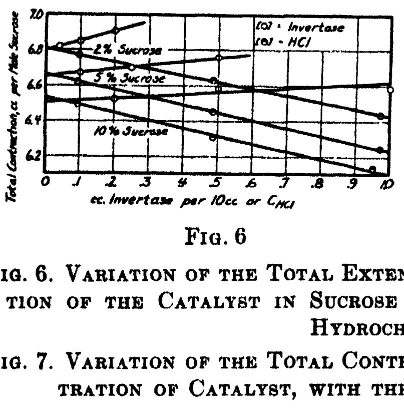

FIG. 6

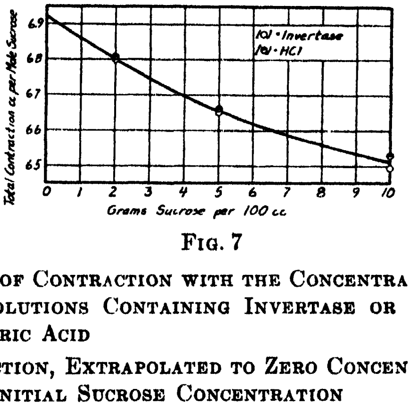

FIG. 7

FIG. 6. VARIATION OF THE TOTAL EXTENT OF CONTRACTION WITH THE CONCENTRATION OF THE CATALYST IN SUCROSE SOLUTIONS CONTAINING INVERTASE OR HYDROCHLORIC ACID

FIG. 7. VARIATION OF THE TOTAL CONTRACTION, EXTRAPOLATED TO ZERO CONCENTRATION OF CATALYST, WITH THE INITIAL SUCROSE CONCENTRATION

The trend of the points plotted in figure 6, however, lends support to a belief in the reality of the variation of the total volume change, because for each sugar concentration the line for acid hydrolysis and that for invertase hydrolysis give nearly the same extrapolated value for the total volume change per mole of sucrose at zero concentration of catalyst. Moreover, these extrapolated values show a regular trend with changes in the initial sucrose concentration, as shown in figure 7. This figure indicates that the volume change accompanying the complete hydrolysis of 1 mole of sucrose in an infinitely dilute solution, with an infinitely small concentration of catalyst, would be about 6.92 cc. This value should correspond to the difference in volume, under these ideal limiting conditions, between 1 mole of sucrose plus 1 mole of water, and 1 mole each of glucose and fructose, after complete mutarotation, at 25°C.

This figure for the volume change at infinite dilution is supported by the following calculations. Riiber (13) found the apparent molar volume of equilibrium glucose at infinite dilution to be 111.06 cc. at 20°C., and that of fructose to be 110.03 cc. The corresponding figure for sucrose has been determined from the density data, also for 20°C., given in the International Critical Tables. A plot of the apparent molar volumes against concentration showed considerable curvature at concentrations below 5 per cent, with a point of inflection at about 1.5 per cent. If the curve is extrapolated from the points for 5 to 25 per cent sucrose, the molar volume at infinite dilution appears to be 210.2 cc., while if the curve is drawn through points for concentrations as low as 0.5 per cent, it appears to be 209.8 cc. Hence this figure may be taken as 210.0 ± 0.2 cc. Since 1 mole of water at 20°C. occupies 18.05 cc., the contraction on the complete hydrolysis of 1 mole of sucrose at 20°C. and at infinite dilution is calculated to be 210.0 ($\pm$0.2) + 18.05 − 111.06 − 110.03, or 6.96 ± 0.2 cc. This agrees much better with the figure found in the present investigation, 6.92 cc. for 25°C., than does the earlier figure of 6.0 cc. for 30°C., reported by Rona (14) and by Sreenivasaya (15). It should be added that the latter authors did not extrapolate to infinite dilution, as they found no definite change of the contraction per mole with changes in concentration.

SUMMARY AND CONCLUSIONS

The rate and extent of the contraction in volume accompanying the hydrolysis of sucrose in solutions containing yeast invertase or hydrochloric acid were measured in dilatometers at 25°C. The volume change in the sucrose-hydrochloric acid solutions was strictly unimolecular, and the velocity constants agreed with those obtained polarimetrically by others. The rate of the volume change in sucrose-invertase solutions, as measured by the reciprocal of the half-period, was directly proportional to the concentration of invertase. The characteristic effects of sucrose concentration and pH on the velocity of invertase action were approximately the same in the dilatometric experiments as in the polarimetric experiments of earlier workers.

The total contraction per mole of sucrose, when the hydrolysis was allowed to go to completion, varied regularly with the concentrations of catalyst and of sucrose, the extreme values observed being about 6.1 and 6.9 cc. From an extrapolation of these values, it was inferred that the complete hydrolysis of 1 mole of sucrose at infinite dilution, to form glucose and fructose in mutarotation equilibrium, would be accompanied by a decrease in volume of about 6.92 cc. at 25°C.

It is concluded that the dilatometric method may be used with confidence in place of the polarimetric method in studying the hydrolysis of sucrose in acid solutions, and that it may also be used in studying invertase action to get a measure of the activity, under optimum conditions, of preparations of yeast invertase.

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THE JOULE-THOMSON EFFECT OF METHANE, NITROGEN, AND MIXTURES OF THESE GASES

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INTRODUCTION

The experimental difficulties of measuring Joule–Thomson coefficients are great and, until fairly recently, too few thermodynamic data (P–V–T and specific heat) of mixtures of gases were available to calculate these coefficients. Although such calculations are tedious, there is little doubt but that the results obtained are certainly as accurate as engineering calculations of design require, and, in many cases, the accuracy of such calculations compares favorably with that of experimentally measured values.

It is the purpose of this paper to present the results of some calculations of the Joule–Thomson coefficients of methane, nitrogen, and mixtures of these gases. The calculations were made originally because of the small amount of actual experimental data available in this field. For the same reason the method will become increasingly important as the liquefaction of gases plays a continually greater rôle in industry. This is particularly true because of the large number of gases to which it may be applied.

THEORETICAL

It is well known that the Joule-Thomson effect, or any other thermodynamic property of a substance, can be readily evaluated if, first, an accurate equation of state representing the pressure–volume–temperature data of the substance is available, and second, if the variation of a pertinent thermal property with temperature is known.

Probably the most accurate and widely applicable equation of state proposed to date is that of Beattie and Bridgeman (3), which reproduces the experimental data of fourteen gases to within 0.1 to 0.2 per cent over a wide range of temperature and pressure. This equation is:

$$P = \frac{RT\,(1 - \epsilon)}{V^2}\,(V + B) - \frac{A}{V^2}$$

where $A = A_0\left(1 - \frac{a}{v}\right), B = B_0\left(1 - \frac{b}{v}\right), \epsilon = \frac{c}{vT^3}$, and A_0, a, B_0, b, and c

are constants specific for each gas, V is volume, P is the pressure, T is the temperature, and R is the gas constant.

In this equation, as in the rest of this paper, the units used are: volume in liters per mole, pressure in atmospheres, and temperature in degrees Kelvin.

Bridgeman (6) utilized this equation of state in deriving an expression for the Joule–Thomson effect based on the thermodynamic relationship

$$\mu C_p = \left(\frac{\partial v}{\partial T}\right)_p - V$$

As a check of this equation he calculated the values for air, and showed that the agreement with the observed values was excellent.

However, this equation was unwieldy and calculations with it were tedious. This led Beattie (2) to attempt several approximations which simplified considerably the final equation without impairing appreciably the accuracy, as was proved by recalculating the values of μ for air.

This latter equation is that used in this paper, since it was sufficiently accurate and was much more convenient to use. The equation is:

$$\mu C_p = \left(-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3}\right) - \left(\frac{2B_0b}{RT} - \frac{3A_0a}{R^2T^2} + \frac{5B_0c}{RT^4}\right)P$$

where μ is the Joule–Thomson coefficient, C_p is the specific heat at constant pressure, and A_0, a, B_0, b, c, R, T, and P are as in the Beattie–Bridgeman equation of state.

CALCULATIONS

The constants A_0, a, B_0, b, and c were calculated for methane and nitrogen by Beattie and Bridgeman and presented in one of their original articles (4). A method of obtaining these constants for mixtures of gases from the constants for the pure gases has been evolved by Beattie (1) and Beattie and Ikehara (5). This is quite simple and merely involves the linear combination of the a's, b's, c's, and B_0's, and squaring the linear combination of the square root of the A_0's.

The constants calculated in this way are as given in table 1.

The constants for the pure gases are those used by Beattie (1) when he showed that the above method of combining constants held for the nitrogen–methane mixtures. Beattie and Bridgeman had also proposed another set of values for nitrogen. Several calculations showed that either set would have been sufficiently exact for the present purpose.

The equation of state for methane reproduced the observed pressures with an average difference of 0.05 per cent over a range of 0 to 200°C. and up to 243 atmospheres. That for nitrogen gave an average deviation of 0.04 per cent in the same temperature range and up to 213 atmospheres.

The sole remaining requirement for the calculation of the Joule–Thomson coefficients is a knowledge of the value of C_p for the pure gases and for the mixture of gases.

Eastman (7) has collected the specific heat data for a number of gases and formulated empirical equations of the form,

$$C_p = \alpha + \beta T + \gamma T^2 + \ldots .$$

to reproduce these data. For methane and nitrogen they are as follows: for methane, $C_p = 5.90 + 0.0096T$; for nitrogen, $C_p = 6.76 + 0.000606T + 0.00000013T^2$. The equation for methane is accurate to only about 5 per cent in the range 150 to 400°K.; and that for nitrogen to about 1.5 per cent in the range 300 to 2500°K.

TABLE 1

Constants calculated for mixtures of methane and nitrogen

Mole per cent CH_4	100	75	50	25	0
Mole per cent N_2	0	25	50	75	100
A	2.2769	1.9575	1.6622	1.3910	1.1440
a	0.01855	0.01838	0.01822	0.01805	0.01788
B	0.05587	0.05269	0.04951	0.04633	0.04314
b	−0.01587	0.01592	0.01598	0.01603	0.01608
c	12.8×10^4	11.02×10^4	9.22×10^4	7.41×10^4	5.60×10^4
R	0.08206	0.08206	0.08206	0.08206	0.08206

C_p, calculated by these equations, is expressed in calories per mole. The factor, 0.0413 liter-atmospheres per calorie, was used to express C_p in liter-atmospheres. The final equations are then:

Methane: $C_p = 0.244 + 0.000396T$
Nitrogen: $C_p = 0.279 + 0.0000250T + 0.0000000054T^2$

By means of linear combination of the coefficients in these equations similar equations for the gas mixtures can easily be obtained.

The calculation of the Joule–Thomson coefficients at atmospheric pressure then becomes relatively simple. However, to calculate the coefficients at other pressures it is necessary to evaluate C_p at these pressures. This can be done by means of another equation derived by Beattie (1a) from thermodynamic relations and the Beattie–Bridgeman equation of state. This equation is:

$$C_p = C_p^* + \left[\frac{2A_0}{RT^2} + \frac{12c}{T^4}\right] P$$

where C_p is the specific heat at absolute temperature T and at pressure P, A_0, c, and R are as in the Beattie–Bridgeman equation of state, and C_p^* is a constant for the given temperature.

C_p^* must be calculated for each temperature at which it is desired to evaluate C_p. This is easily done, since C_p can be calculated from the usual equations at 1 atmosphere, after which substitution will permit solving for C_p^*. With C_p^* known for a certain temperature, C_p can be evaluated for any pressure at this temperature. This same method applies to gas mixtures if the constants for the Beattie–Bridgeman equation of state and the C_p equations are known.

These calculations of the Joule–Thomson coefficients can be systematized so that the process is not so long and tedious as it would at first appear to be.

DISCUSSION OF RESULTS

The results with the pure gases and the three mixtures are given in table 2. The lower temperatures are outside the range for which the original equations were derived, but it is believed that because of the excellent agreement between the observed and the calculated P–V–T data in the given range the extrapolation does not introduce serious error when taking into account the accuracy of the calculations as a whole.

The original calculations were made principally for engineering purposes, so that the accuracy of the calculated values did not have to be of an extremely high order. The accuracy in the calculations was limited by the accuracy of the available specific heat equations, which, in the case of methane, was not very great.

Pure gases

For the purpose of comparison, the few available data on the Joule–Thomson effect for methane and nitrogen are given below. The agreement between the observed and calculated data for methane is quite good, but that for nitrogen is very poor. Inasmuch as the equation of state for nitrogen fitted the P–V–T data so well and gave such good results in the calculations of the equations of state of mixtures, it is believed that the older observed data are probably at fault. Because of the difficulty of the experimental determinations of Joule–Thomson coefficients this is not surprising.

Gas mixtures

An examination of the equations for the Joule–Thomson coefficients will reveal the fact that with the given method of combining constants the coefficients for gas mixtures should be obtainable for most purposes by a linear combination of the coefficients of the pure gases. An examination of table 2 will indicate that this is true within the accuracy of the calculations.

USE OF FIGURES 1 AND 2

The isotherms for the pure gases are given in figures 1 and 2. To estimate the Joule–Thomson coefficients for any mixture, it is only necessary

TABLE 2

Joule-Thomson coefficients of nitrogen-methane mixtures

PRESSURE IN ATMOSPHERES	JOULE-THOMSON COEFFICIENTS				
	200°K	250°K	300°K	350°K	400°K.
(a) 100 per cent CH_4					
1	0.88	0.58	0.41	0.30	0.23
5	0.85	0.57	0.40	0.30	0.22
25	0.73	0.51	0.37	0.28	0.21
50	0.62	0.46	0.34	0.26	0.20
100	0.46	0.37	0.28	0.22	0.17
(b) 75 per cent CH_4 and 25 per cent N_2					
1	0.77	0.50	0.36	0.26	0.20
5	0.74	0.49	0.35	0.26	0.19
25	0.65	0.45	0.33	0.24	0.18
50	0.55	0.40	0.30	0.22	0.17
100	0.41	0.34	0.25	0.19	0.15
(c) 50 per cent CH_4 and 50 per cent N_2					
1	0.65	0.43	0.31	0.22	0.17
5	0.64	0.42	0.30	0.22	0.16
25	0.56	0.39	0.26	0.21	0.15
50	0.48	0.35	0.26	0.19	0.14
100	0.37	0.28	0.21	0.16	0.12
(d) 25 per cent CH_4 and 75 per cent N_2					
1	0.54	0.36	0.25	0.18	0.14
5	0.53	0.35	0.25	0.18	0.13
25	0.47	0.33	0.23	0.17	0.13
50	0.41	0.29	0.21	0.16	0.11
100	0.32	0.24	0.17	0.13	0.09
(e) 100 per cent N_2					
1	0.44	0.29	0.20	0.15	0.10
5	0.43	0.28	0.20	0.14	0.10
25	0.38	0.26	0.18	0.13	0.09
50	0.33	0.23	0.17	0.12	0.08
100	0.26	0.19	0.14	0.10	0.07

Joule-Thomson effect data from International Critical Tables, Vol. V, pp. 144–6

For CH_4, $\mu = t_1 - t_0/p - 1$ in °C. per atmosphere ± ca. 0.05

p	25	17	14.6	27	55
t_1 in °C. . . .	−77	−78	−78	−10	10
μ . . .	0.75	0.75	0.74	0.35	0.40

For N_2, μ in °C. per atmosphere

°C.. .	0	20	40	60	80	100
μ .	0.333	0.291	0.250	0.215	0.187	0.159

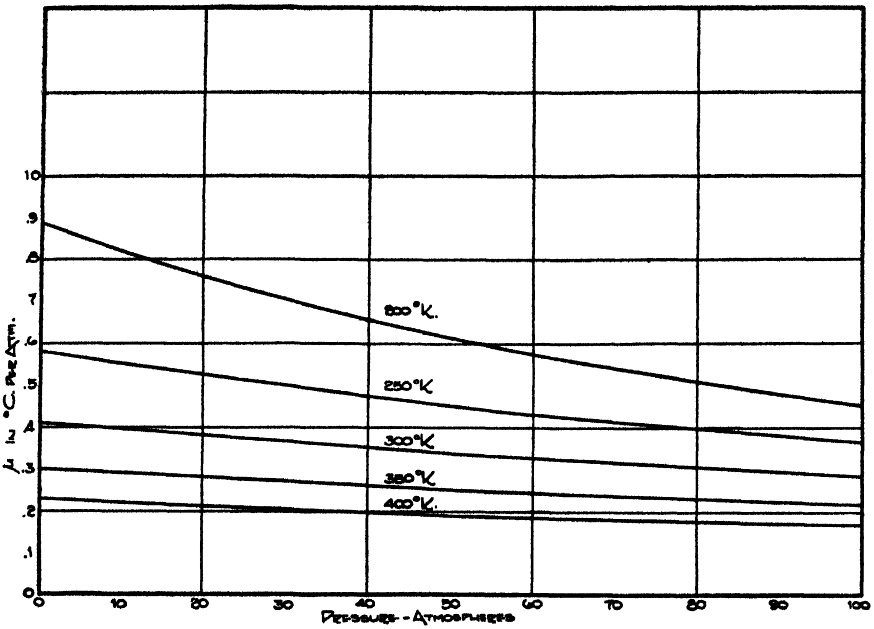

Fig. 1. The Joule-Thomson Effect for Methane

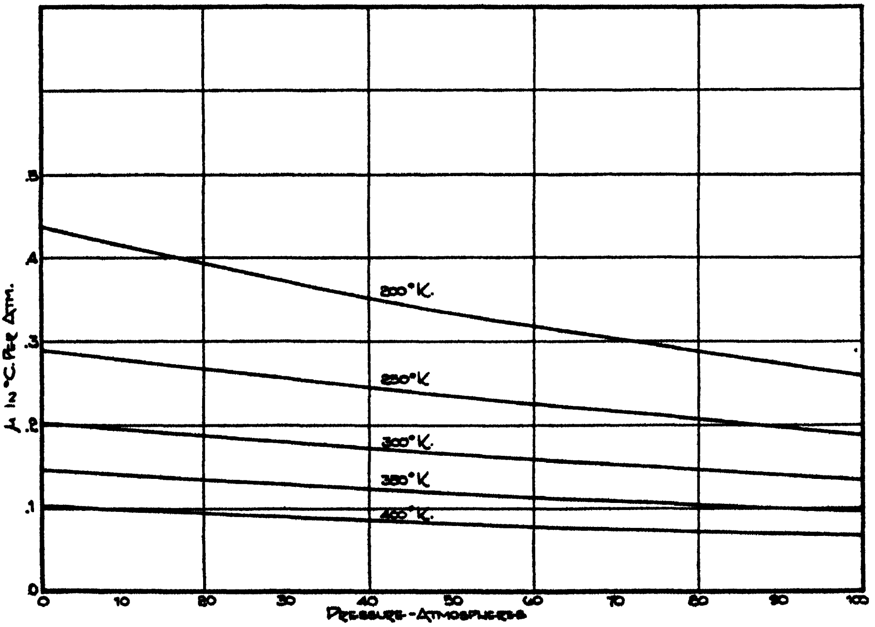

Fig. 2. The Joule-Thomson Effect for Nitrogen

to combine linearly the values for the pure gases as obtained from these curves. Since μ is the change of temperature with pressure, a positive sign indicates that a decrease in pressure will be accompanied by a decrease in temperature.

CONCLUSIONS

The Joule-Thomson coefficients of methane and nitrogen have been calculated at the temperatures 200, 250, 300, 350, and 400°K. and pressures of 1, 5, 25, 50, and 100 atmospheres, using the Beattie-Bridgeman equation of state. A method of obtaining the coefficients for mixtures of these gases from those of pure gases has been indicated, and data for three mixtures of these gases have been calculated and tabulated.

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THE COMPARATIVE ACTION OF MIXED CATALYSTS WHEN USED FOR THE JOINT DEHYDRATION OF ETHYL ALCOHOL AND AMMONIA. I

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Sabatier and Mailhe (8) were the first to indicate the possibility of obtaining alkylamines by the interaction of alcohol and ammonia in the presence of such dehydrating catalysts as thoria or alumina. Subsequently, many investigators studied quantitatively the process of the catalytic alkylation of ammonia.

Eug. and Kaz. Smolensky (9) passed ammonia gas and vapors of ethyl alcohol over alumina at temperatures of 330–350°C. and obtained a mixture of three amines with a yield of 53 per cent, based on the ethyl alcohol that had entered the reaction, and, as by-products, ethyl ether and ethylene. When the molecular ratio $NH_3:C_2H_5OH$ was 1:2, the mixture consisted of 15 per cent of mono-, 70 per cent of di-, and 15 per cent of trimethylamine.

Brown and Reid (3) studied the joint catalytic dehydration of ammonia and methyl, ethyl, *n*-propyl, and *n*-butyl alcohols. These authors tried not only individual catalysts, such as blue tungsten oxide and silica gel, but also mixed catalysts, such as the following: alumina on pumice, mixtures of silica gel and nickel oxide, cerium oxide on pumice, and mixtures of silica gel and thorium oxide. The best catalyst among those mentioned above proved to be a silica gel prepared in a special way. At 465°C., with this catalyst, 39.5 per cent of ethyl alcohol was converted into a mixture of amines in the ratio 2:5:3.

Dorrell (4) studied the influence of temperature, contact time, and ratio of ethyl alcohol to ammonia in the presence of alumina. The best yield was obtained at 344°C. In runs where a relatively large amount of alcohol was taken, there was an increase in the yield of the secondary amine. A decrease in the velocity of the initial products (an increase of the contact time) led to a decomposition of the amines into ammonia and ethylene.

A similar investigation was carried out with methyl alcohol by Briner and Gandillon (2). The authors studied the catalytic activity of alumina, thoria, silica gel, kaolin, and blue tungsten oxide. The catalysts are reported in the order of their decreasing activity in the reaction of the methylation of ammonia. In the presence of alumina at 405°C., with a volume ratio $NH_3:CH_3OH = 2.25:1$, a mixture of amines was obtained with a yield of 52.7 per cent. The content of the different amines in the mixture was as follows: methylamine, 43 per cent; dimethylamine, 36 per cent; and trimethylamine, 31 per cent. A decrease in the contact time led to an increased yield of the primary amine and to the decomposition of the secondary and tertiary compounds.

All the authors quoted above have investigated only the action of individual catalysts. Only in a few separate runs by Brown and Reid (3) have mixed catalysts been tried. The most effective one proved to be a mixture of silica gel and thoria. Up to now there have been no investigations dealing with the comparative action of mixed catalysts in the alkylation reaction of ammonia by means of alcohols.

The present investigation had for its purpose the study of the dehydrating action of mixtures, consisting of alumina and of iron, chromium, tin, and zinc oxides, and the comparison of the activity of these mixtures with that of pure alumina, which has proved to be, according to former investigations, a highly active catalyst for the dehydration of the system alcohol–ammonia.

It seemed interesting also to find out how catalysts consisting of alumina and of tin or zinc oxide would behave in this case, taking into consideration that the latter two substances in a pure state are catalysts of complex action, with a considerable predominance of dehydrogenating over dehydrating properties.

In the present paper, the following catalysts were investigated:[1] (1) alumina; (2) Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent); (3) Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent); (4) Al_2O_3 (90 per cent) + SnO (10 per cent); (5) Al_2O_3 (90 per cent) + ZnO (10 per cent).

In our former investigation, dealing with the hydration of diethyl ether under pressure (1), mixtures of zinc and iron oxides with alumina proved to be more active than pure alumina.

EXPERIMENTAL PART

A. Preparation of catalysts

Aluminum hydroxide and the mixture consisting of aluminum hydroxide (90 per cent) and iron hydroxide (10 per cent) were prepared as described in a previous paper dealing with the hydrolysis of diethyl ether (1). The catalyst, consisting of Al_2O_3 (80 per cent) and Cr_2O_3 (20 per cent), was prepared by precipitating a solution containing 750.3 g. of $Al(NO_3)_3 \cdot 9H_2O$

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[1] All the oxides used were hydrated oxides.

and 134.2 g. of $Cr(NO_3)_3 \cdot 9H_2O$ with a 25 per cent solution of ammonium hydroxide, the mixture being vigorously stirred all the time.

The catalyst containing Al_2O_3 (90 per cent) and SnO (10 per cent) was prepared as follows: To a solution of 664.4 g. of $Al_2(SO_4)_3 \cdot 18H_2O$ and 18.1 g. of $SnSO_4$, sodium hydroxide was added with stirring until the dissolution of the hydroxides that appeared at first. Then sulfuric acid was added until the disappearance of the alkaline reaction to litmus.

In order to obtain the catalyst consisting of Al_2O_3 (90 per cent) and ZnO (10 per cent), two separate solutions were prepared, one containing 750.3 g. of $Al(NO_3)_3 \cdot 9H_2O$, and the other 41.4 g. of $Zn(NO_3)_2 \cdot 6H_2O$. These two solutions were added separately to a concentrated solution of sodium hydroxide until the precipitates completely disappeared. The aluminate and zincate solutions were then mixed together and nitric acid added to the mixture until the alkaline reaction to litmus disappeared.

In the preparation of all of these catalysts, the precipitates were carefully washed with hot water until a negative test for the corresponding anion was obtained, then they were dried at 150°C. and fragments of the size of an average pea were used.

B. Experiments on joint dehydration of ammonia and ethyl alcohol

These experiments were carried out at temperatures of 300, 330, 360, and 400°C. The apparatus consisted of a glass reaction tube, having a diameter of 15 mm., and placed in an electric furnace. The catalyst, dried at 150°C., was packed in a 30-cm. section of the tube.

The alcohol was added from a graduated buret, and the ammonia (Schering-Kahlbaum) was taken from a bomb and passed first through a flask filled with lumps of sodium hydroxide for drying purposes. The rate at which the ammonia was added was measured by a flowmeter filled with alcohol. In different runs this rate varied from 55 to 60 cc. per minute. The alcohol was added in all runs at a rate of 1.6 cc. per 10 minutes. Twenty cubic centimeters of alcohol was passed over the catalyst in each run. The molecular ratio $NH_3:C_2H_5OH$ was about equal to 1.

The condensate was collected in three consecutive receivers. The last two were provided with coils and placed in a cooling mixture. The gases, after passing the last receiver, were collected in a graduated gasometer over water, where their volume could be measured with a precision up to 5 cc. The largest amount of condensate was collected in the first receiver.

Products obtained in the experiments with the catalysts $Al_2O_3 + Cr_2O_3$ and $Al_2O_3 + ZnO$ at 360 and 400°C., had a characteristic odor of pyridine bases. Probably in the above experiments there was a side reaction consisting in the dehydrogenation of alcohol with the formation of the corresponding aldehyde, and this aldehyde condensed with ammonia giving α- or β-picolines. These products were obtained under similar conditions by Tschitschibabin (10).

C. The analysis of reaction products

The analysis of the reaction products was effected by using a modification of the methods of François (6) and Erdmann (5). All the condensate was neutralized with dilute (1:1) hydrochloric acid under cooling. The condensate from those receivers that had been cooled during the experiment was distilled into a flask containing dilute acid (figure 1), first by heating each receiver with the hand and then by heating on a warm water bath. The liquid that did not distil under these conditions was neutralized in the receiver.

The solution of amine hydrochloride was placed in a citrate bottle of 400-cc. capacity, and a mixture consisting of equal volumes of a saturated soda solution and a 20 per cent sodium hydroxide solution was added in excess. Then 70 g. of ground yellow mercuric oxide was also added to the mixture. The mixture was shaken on a mechanical shaker for one hour and then was left standing for twenty hours. The solution was filtered from the precipitate and the latter was washed three times with small quantities of water.

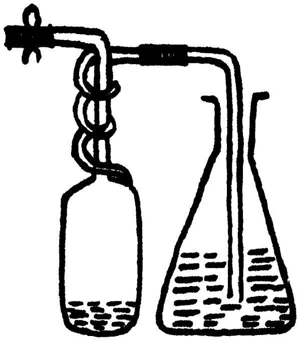


FIG. 1

The mixture of amines was distilled and collected in a 0.2 *N* hydrochloric acid solution; the excess of acid was titrated with a 0.1 *N* sodium hydroxide solution in the presence of methyl red.

In all experiments only the total amine content was determined. The catalyst was heated before the experiment to 400°C. until the elimination of water ceased, and then before every experiment ammonia was passed over the catalyst for thirty to forty minutes.

DISCUSSION OF RESULTS

The results of our experiments on the joint catalytic dehydration of ethyl alcohol and ammonia are reported in table 1. The catalysts are given in the first column in the order of their decreasing activities for this process at 400°C. In the second column the temperature of the experiments is reported. In the third the yields of the amines, expressed in cubic centimeters of a 0.1 *N* hydrochloric acid solution that was used for the neutralization of these amines. In the fourth column the decomposition of the alcohol is expressed in percentage calculated on the basis of the gas collected in the gasometer.

TABLE 1

Catalytic dehydration of ethyl alcohol and ammonia

CATALYST	TEMPERATURE OF THE EXPERIMENT	AMOUNT OF 0.1 *N* HCl USED FOR THE NEUTRALIZATION OF THE AMINES	ALCOHOL DECOMPOSED
	°C.	*cc.*	*per cent*
Al_2O_3	300	516.7	8.9
	330	520.9	12.6
	360	570.3	15.9
	400	727.7	23.5
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	300	82.0	1.8
	330	215.5	2.6
	360	579.0	3.9
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	400	725.8	12.5
Al_2O_3 (90 per cent) + ZnO (10 per cent)	300	90.3	2.0
	330	96.0	4.3
	360	247.4	9.6
	400	319.2	27.1
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)	300	219.2	4.0
	330	287.7	12.3
	360	275.9	46.6
	400	195.4	70.2
Al_2O_3 (90 per cent) + SnO (10 per cent)	300	283.7	1.5
	330	300.9	4.0
	360	408.6	11.6
	400	141.6	41.1

From table 1 we may see that the mixed catalysts used by us, if compared with pure alumina, do not seem to accelerate the reaction of ethylation of ammonia with ethyl alcohol. The only exception is the mixture $Al_2O_3 + Fe_2O_3$, which at 360°C. as well as at 400°C. gives practically the same yield as pure alumina. Besides, it is necessary to note the small activity of this catalyst in the decomposition of alcohol. This fact distinguishes it in the process from all other catalysts.

In the case of pure alumina and a mixture of the latter with ferric oxide and zinc oxide, the yield of amines in the interval between 300 and 400°C. increases with the rise of temperature, whereas in the case of the catalyst $Al_2O_3 + SnO$ a maximum yield was obtained at 360°C., and in the case of $Al_2O_3 + Cr_2O_3$ at 330°C. The latter catalyst showed at 360 and 400°C. an extremely high activity in the direction of alcohol decomposition, and a small activity in the ethylation of ammonia.

The catalysts can be arranged as follows in order of their decreasing activity in the reaction of the decomposition of alcohol at 400°C.: $Al_2O_3 + Cr_2O_3$; $Al_2O_3 + SnO$; $Al_2O_3 + ZnO$; Al_2O_3; $Al_2O_3 + Fe_2O_3$.

As we should have expected, the percentage of alcohol decomposition increases with the rise of temperature. In the case of alumina this increase is almost a linear function.

According to Sabatier (8; cf. ref. 7), if we have pure alumina or pure chromium oxide and pass over them ethyl alcohol and ammonia, these catalysts will decompose ethyl alcohol only slightly with the formation of ethylene and water, because the chief reaction would be the formation of an amine. But when in our case we added to alumina 20 per cent of chromium oxide, the chief reaction was already the decomposition of the alcohol (at 360°C., 46.6 per cent; at 400°C., 70.2 per cent).

Likewise, a catalyst consisting of alumina and 10 per cent of tin suboxide decreases the rate of the reaction of ethylation of ammonia fivefold at 400°C., and increases the decomposition rate of the alcohol nearly twice.

Alumina to which 10 per cent of zinc oxide has been added lowers considerably the rate of both possible processes,—the ethylation of ammonia as well as the decomposition of the alcohol—particularly in the interval 300–330°C.

The catalyst consisting of alumina to which 10 per cent of iron oxide has been added influences the reaction of the ethylation of ammonia in the 360–400°C. range, in the same way as pure alumina, considerably decreasing the process of alcohol decomposition (at 360°C., four times; at 400°C., nearly twice).

The catalytic action of these mixed catalysts shows that their properties are different from the properties of oxides of which these mixtures are made, and also that apparently they can even change the direction of the reaction.

The results thus obtained are of interest from still another point of view.

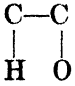
In a previous paper[2] it was shown that a great number of reactions could be expressed by means of structural matrices:

$$\Phi_2 = \begin{Vmatrix} \varphi_{11} & \varphi_{12} & \varphi_{13} \\ \varphi_{21} & \varphi_{22} & \varphi_{23} \\ \varphi_{31} & \varphi_{32} & \varphi_{33} \end{Vmatrix}$$

where φ_{11}, φ_{31}, φ_{33}, and φ_{13} correspond to atoms in the molecule that come in contact with the catalyst, φ_{12}, φ_{21}, φ_{32}, and φ_{23} correspond to bonds, and $\varphi_{22} = 0$.

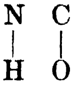
In a study of catalysis, one of the chief problems is to find a relation between these matrices (indexes) and the nature of the catalyst.

Such a relation may really be observed, but it has been but very poorly traced in the case of a systematic change of separate elements. In our case we can select the following elements for comparison. These elements are separate members of the complete system that was found previously:



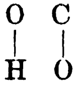
$$\begin{array}{c} \mathrm{C}-\mathrm{C} \\ | \quad\; | \\ \mathrm{H} \quad \mathrm{O} \end{array}$$

$\mathrm{II}\,K^2_{17}\,3$



$$\begin{array}{c} \mathrm{N} \quad \mathrm{C} \\ | \quad\; | \\ \mathrm{H} \quad \mathrm{O} \end{array}$$

$U(\mathrm{II}\,K^2_1\,1)$[3]

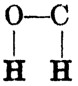


$$\begin{array}{c} \mathrm{O} \quad \mathrm{C} \\ | \quad\; | \\ \mathrm{H} \quad \mathrm{O} \end{array}$$

$\mathrm{II}\,K^3_{43}\,1$

As may be seen, the difference consists only in the elements φ_{11} (C, N, and O), which change according to the order of their atomic numbers (the difference in φ_{12} has only a subordinate significance).

For catalysts to be compared we take the type of mixed catalysts where one of the components is aluminum hydroxide, which, as is already known, facilitates the reaction having the index II K^2_{17} 3, and the other component is such a metallic oxide as catalyzes the dehydrogenation of alcohols:



$$\begin{array}{c} \mathrm{O}-\mathrm{C} \\ | \quad\; | \\ \mathrm{H} \quad \mathrm{H} \end{array}$$

$U(\mathrm{II}\,K^2_3\,2)U$

The latter index differs from index II K^3_{43} 1 by the elements φ_{33}: in II K^3_{43} 1, φ_{33} corresponds to an oxygen atom, and in the case of dehydrogenation φ_{33} corresponds to a hydrogen atom.

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[2] The terminology in the present paper is taken from the article referred to (see Balandin: J. Phys. Chem. U. S. S. R. **5**, 679–706 (1934).

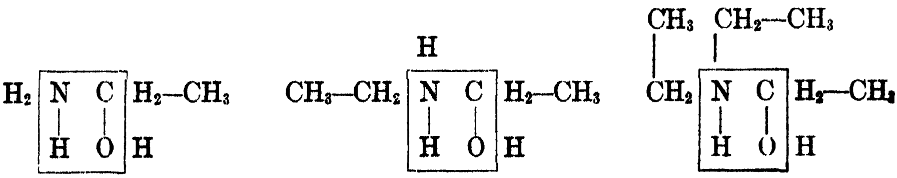
[3] Below the index its symbol is given; when multiplied by matrix

$$U = \begin{Vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{Vmatrix}$$

the index does not change, but only turns.

Experiments (1) have shown that such mixed catalysts accelerate considerably reactions belonging to class II K_{48} 1 (ether hydrolysis). The reaction II K^2_{17} 3 (alcohol dehydration), it seems, is not sensitive towards the addition of dehydrogenating oxides to alumina.

The reaction studied in the present paper, the joint dehydration of ethyl alcohol and ammonia, is one of the cases of index *U*(I K^2_1 1), which occupies a middle position in the above-mentioned series. This applies not only to the first stage, the formation of a primary amine, but also to subsequent reactions,—to the formation of a secondary and tertiary amine:

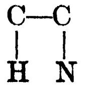


$$H_2\boxed{\begin{matrix}N & C\\ | & |\\ H & O\end{matrix}}\begin{matrix}H_2{-}CH_3\\ \\ H\end{matrix}\qquad CH_3{-}CH_2\boxed{\begin{matrix}\overset{H}{N} & C\\ | & |\\ H & O\end{matrix}}\begin{matrix}H_2{-}CH_3\\ \\ H\end{matrix}\qquad \begin{matrix}CH_3\\ |\\ CH_2\end{matrix}\boxed{\begin{matrix}\overset{\overset{CH_2-CH_3}{|}}{N} & C\\ | & |\\ H & O\end{matrix}}\begin{matrix}H_2{-}CH_3\\ \\ H\end{matrix}$$

In order that such a reaction may take place upon the same active centers of the catalysts on which the alcohol dehydration reaction took place, it is necessary for the alcohol molecule to turn somewhat, i.e., to be oriented in a different way, so that the places previously occupied by atoms $\begin{matrix}C\\ |\\ H\end{matrix}$ and now left free in the left part of the index, should be occupied by the group $\begin{matrix}N\\ |\\ H\end{matrix}$. It appears that in such a case the addition of dehydrogenating oxides to alumina decreases the rate of the reaction, in contrast to the case of ether hydrolysis. In that instance we can see how profoundly specific is the action of a catalyst, even when the reactions are very similar. The introduction of a nitrogen atom instead of oxygen into the index already produces a perturbation in the catalytic activity.

According to previous theories, the reactions of ether hydrolysis as well as of the amination of an alcohol were considered as representing one and the same type of reaction, namely, the reaction of addition or removal of water. It was considered that only the elements of water come into a temporary contact with the catalyst. From the point of view of these old theories it was not possible to expect a difference in the catalyst action. From the point of view of the new theory, where the interaction of *all* the atoms participating in the reaction is taken into consideration, such a difference cannot readily be unexpected.

We should remark still further that the addition of iron oxide decreases the rate not only of reactions II K^2_{17} 3, but also of an analogous reaction,—the splitting of the amine that was formed,



$$\begin{array}{cc} C & \!\!—\!\! C \\ | & | \\ H & N \end{array}$$

II K^2_{16} 4

which differs from the former reaction only by φ_{33} (φ_{33} corresponds to an oxygen atom in II K^2_{17} 3, and to a nitrogen atom in II K^2_{16} 4). The specific action of the catalyst in this case is manifested just as sharply as in previous cases.

CONCLUSIONS

1. Mixed catalysts studied by us (except $Al_2O_3 + Fe_2O_3$ at 360°C. and 400°C.), when compared to pure alumina, under the conditions of our experiments, decrease the reaction rate of the formation of amines from ethyl alcohol and ammonia.

2. Among the mixed catalysts that we tried, the most effective one proved to be a catalyst consisting of 90 per cent Al_2O_3 and 10 per cent Fe_2O_3. The advantage of this catalyst over pure alumina consists in a smaller decomposition of the alcohol in its presence.

3. The action of mixed catalysts in this case is not an additive one.

4. The facts observed are interpreted from the point of view of the multiplet theory.

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COMPARATIVE ACTION OF MIXED CATALYSTS WHEN USED FOR THE JOINT DEHYDRATION OF ETHYL ALCOHOL AND ANILINE. II

CATALYTIC PREPARATION OF MONOETHYLANILINE

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In our former paper (9) we have investigated the action of mixed catalysts in the joint dehydration of ethyl alcohol and ammonia with the formation of corresponding amines. In connection with this it appeared interesting to test the efficiency of the same catalysts (see below) in the joint dehydration of aniline and ethyl alcohol with the formation of mono- and diethylaniline and to compare their action with the activity in this process of pure alumina. We have also tested a catalyst consisting of 95 per cent alumina and 5 per cent nickel oxide, which had proved to be very active in the hydrolysis of diethyl ether under pressure (2).

The possibility of obtaining alkylanilines by means of heterogeneous catalysis under ordinary pressure was for the first time established by Mailhe and de Godon (7). These authors passed methyl alcohol and aniline over alumina at 400–430°C. and obtained methylaniline and from it, by a further action of methyl alcohol, dimethylaniline. In the presence of the same catalyst, from *o*-, *m*-, and *p*-toluidines and methyl alcohol at 350–400°C., they obtained (8) a mixture of nearly equal amounts of the corresponding secondary and tertiary amines.

Mailhe in his patent (6) concerning the preparation of a series of arylamines, among them ethyl- and diethyl-aniline, recommends the following catalysts: Al_2O_3, ThO_2, and ZrO_2. For the reaction between ethyl alcohol and aniline he proposes alumina at a temperature of 350–400°C.

E. and K. Smolensky (10) claim that by passing twice a mixture of methylaniline with methyl alcohol over alumina at 300°C. they obtained dimethylaniline with a yield of 95 per cent. By passing aniline and methyl alcohol over silicon dioxide at 300–320°C., monomethylaniline could be obtained.

Brown and Reid (3) have investigated the catalytic action of silica gel in the reaction of the ethylation of aniline with alcohol. They found that at a temperature of 385°C. (using a molar ratio aniline:alcohol = 1:1.05) a mixture of secondary and tertiary amines was obtained with a ratio of 5:1 and a yield of 41.5 per cent. Using the same temperature but a molar ratio aniline:alcohol = 1:2.05 they obtained 46.6 per cent of ethylaniline and 13.3 per cent of diethylaniline (ethylaniline:diethylaniline = 77:2); the catalyst rapidly lost its activity.

In later papers the joint dehydration of methyl alcohol and aniline was investigated only in the presence of "Japanese acid earth" (5) (its composition after washing with water and drying in the air: SiO_2, 61.67 per cent; Al_2O_3, 12.28 per cent; Fe_2O_3, 1.87 per cent; CaO, 0.16 per cent; MgO, 3.44 per cent; loss after drying at 110°C., 15.66 per cent; loss after heating to incandescence, 4.64 per cent) and in the presence of thorium oxide (4).

The joint dehydration of ethyl alcohol and aniline in the presence of mixed catalysts has not as yet been investigated.

It must be remarked that the study of mixed catalysts used for the alkylation of aromatic amines has not only a purely theoretical interest, but also a practical one, because it gives the necessary data concerning the influence of impurities upon the action of catalysts in industrial processes.

The following catalysts have been tested in our experiments:[1] (1) Al_2O_3; (2) Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent); (3) Al_2O_3 (90 per cent) + SnO (10 per cent); (4) Al_2O_3 (90 per cent) + ZnO (10 per cent); (5) Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent); (6) Al_2O_3 (95 per cent) + NiO (5 per cent).[2]

EXPERIMENTAL PART

Experiments on the joint catalytic dehydration of aniline and ethyl alcohol were performed with each of the above-mentioned catalysts at temperatures of 350, 375, and 400°C.

The apparatus consisted of a tube of hard glass having a 15 mm. interior diameter into which the catalyst was placed. The catalyst was in the form of small lumps dried at 150°C. The tube was placed in an electric furnace and was provided at its front end with a special buret (1) for a regular introduction of a mixture of alcohol and aniline, and at the rear end with a receiver that was cooled with ice. The length of the catalyst layer in all experiments was 48 cm.

In every experiment the same mixture was used, consisting of 86 g. of pure, freshly distilled aniline (b.p. 182.5–183.5°C., $n_D^{20°}$ 1.5864) and 64 g. of 96 per cent rectified ethyl alcohol ($d_4^{15°}$ 0.8056).

The molecular ratio aniline:alcohol was about 2:2.9. The mixture of aniline and alcohol was introduced into the reaction tube regularly, at a rate of 12 cc. per hour, and was passed over the catalyst once. As all the experiments were of a comparative nature, the same conditions were maintained in all cases where this was possible.

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[1] The description of their preparation is given in the preceding paper by Shuykin, Balandin, and Plotkin (9). All the catalysts were actually hydroxides.

[2] For the preparation of this catalyst see reference 9.

In all the experiments at a temperature of 300°C. the color of the condensate was light yellow; with the rise of the temperature a change of color to orange-yellow was observed.

The condensates obtained were separated from the water–alcohol layer and dried over melted sodium hydroxide. The product was fractionated twice with a Vigreux column (sixteen sections, length 58 cm.), which was heated by means of electricity to a constant temperature. An insignificant quantity of the product which distilled up to 160°C. consisted of ether, of alcohol that had not entered into the reaction, of water, and of traces of aniline. This fore-run was not taken into account.

TABLE 1

Indices of refraction of mixtures

ANILINE	ETHYLANILINE	$n_D^{20°}$ OF THE MIXTURE	ETHYLANILINE	DIETHYLANILINE	$n_D^{20°}$ OF THE MIXTURE
per cent	*per cent*		*per cent*	*per cent*	
100	0	1.5864	100	0	1.5557
90	10	1.5812	90	10	1.5543
80	20	1.5781	80	20	1.5528
70	30	1.5753	70	30	1.5516
60	40	1.5722	60	40	1.5503
50	50	1.5693	50	50	1.5490
40	60	1.5663	40	60	1.5477
30	70	1.5637	30	70	1.5466
20	80	1.5607	20	80	1.5453
10	90	1.5580	10	90	1.5440
0	100	1.5557	0	100	1.5424

The following fractions were collected: I, 160–195°C.; II, 195–210°C.; and III, 210–230°C. In the flask there remained a small quantity of a liquid, boiling above 230°C., which was not investigated further.[3] Fraction I (160–195°C.) consisted of a mixture of aniline and ethylaniline; fraction II (195–210°C.) of aniline, ethylaniline, and traces of diethylaniline; fraction III (210–230°C.) of ethylaniline and diethylaniline.

For each fraction the indices of refraction were determined. In order to determine the composition of these fractions by the indices of refraction, two series of synthetic mixtures were prepared consisting (a) of aniline and ethylaniline and (b) of ethylaniline and diethylaniline, taken in different percentages by weight (see table 1). The initial substances (Kahl-

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[3] The residues from all experiments were collected and fractionated. The product boiled from 230 to 271°C. and gave a negative reaction for the presence of diphenylamine.

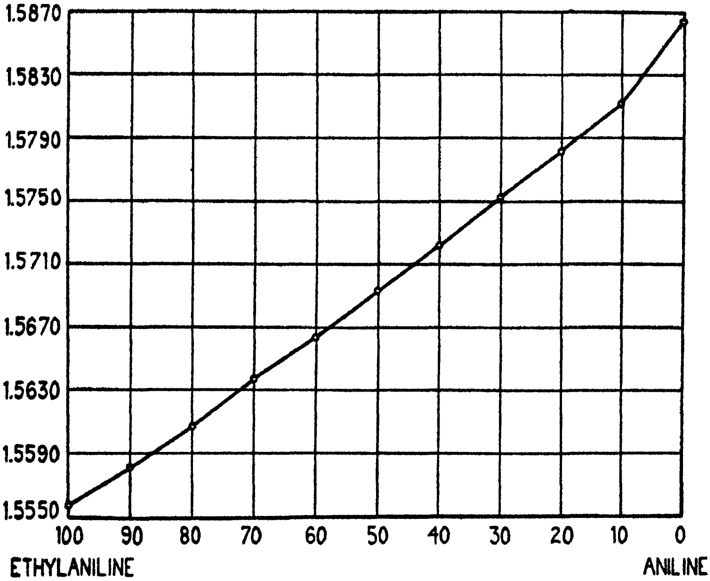


FIG. 1. DEPENDENCE OF INDEX OF REFRACTION ON THE COMPOSITION OF THE MIXTURE

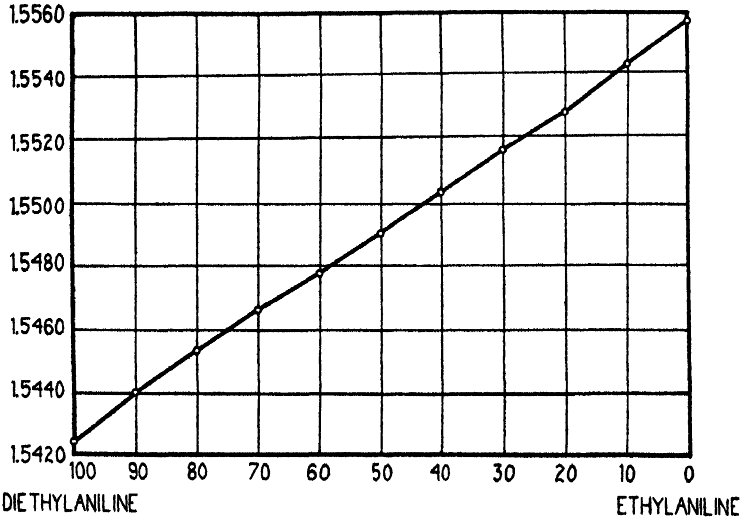


FIG. 2. DEPENDENCE OF INDEX OF REFRACTION ON THE COMPOSITION OF THE MIXTURE

baum) were previously distilled twice: aniline, b.p. 182.5–183.5° at 751 mm., $n_D^{20°}$ 1.5864; ethylaniline, b.p. 203–204°C. at 754 mm., $n_D^{20°}$ 1.5557; diethylaniline, b.p. 214.5–215.5°C. at 754 mm., $n_D^{20°}$ 1.5424.

TABLE 2

Alkylation of aniline

CATALYSTS	TEMPERATURE OF EXPERIMENT	WEIGHT OF CRUDE CONDENSATE	NO. OF FRACTIONS	WEIGHT OF FRACTIONS	$n_D^{20°}$ OF FRACTIONS	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF MONOETHYLANILINE	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF DIETHYLANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	LOSS OF ALCOHOL
	°C.	grams		gm.		per cent	per cent	per cent	per cent
Al_2O_3	350	140	1	30	1.5631	64 3	3 2	67.5	26 7
			2	60	1 5556				
			3	7	1 5474				
	375	136	1	19	1 5679	51 4	3 5	54.9	37.4
			2	50	1 5581				
			3	7	1 5468				
	400	135	1	22	1 5728	41 8	7 1	48 9	40 1
			2	37	1.5581				
			3	15	1.5471				
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent). . .	350	142	1	28	1 5727	48 0	2.1	50.1	21 4
			2	39	1 5556				
			3	7	1 5502				
	375	140	1	32	1 5700	52 2	0 7	52.9	26.7
			2	42	1 5576				
			3	6	1 5528				
	400	132	1	52	1.5732	39 4		39.4	48 1
			2	25	1 5595				
			3	4	1.5557				
Al_2O_3 (90 per cent) + SnO (10 per cent)........ ..	350	137	1	25	1 5748	45 6	2 8	48 4	34.7
			2	39	1 5562				
			3	9	1 5500				
	375	136	1	25	1.5735	48 7	1.5	50.2	37.4
			2	46	1.5550				
			3	4	1 5486				
	400	135	1	40	1 5703	44 0	0.3	44.3	40.1
			2	31	1.5579				
			3	3	1.5540				

TABLE 2—*Concluded*

CATALYSTS	TEMPERATURE OF EXPERIMENT	WEIGHT OF CRUDE CONDENSATE	NO. OF FRACTIONS	WEIGHT OF FRACTIONS	$n_D^{20°}$ OF FRACTIONS	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF MONOETHYLANILINE	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF DIETHYLANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	LOSS OF ALCOHOL
	°C.	*grams*		*gm.*		*per cent*	*per cent*	*per cent*	*per cent*
Al_2O_3 (90 per cent) + ZnO (10 per cent)	350	141	1	60	1.5750	31.6	Traces	31.6	24.1
			2	18	1.5631				
			3	4	1.5556				
	375	132	1	52	1.5744	29.7		29.7	48.1
			2	14	1.5646				
			3	8	1.5586				
	400	133	1	66	1.5796	18.9		18.9	45.4
			2	14	1.5689				
			3	4	1.5610				
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)	350	132	1	58	1.5726	34.9	0.6	35.5	48.1
			2	16	1.5580				
			3	3	1.5518				
	375	136	1	47	1.5726	43.2	Traces	43.2	37.4
			2	31	1.5578				
			3	2	1.5553				
	400	126	1	54	1.5773	24.4		24.4	64.2
			2	16	1.5620				
			3	3	1.5571				
Al_2O_3 (95 per cent) + NiO (5 per cent)	350	138	1	53	1.5720	38.4	0.1	38.5	32.1
			2	20	1.5600				
			3	5	1.5554				
	375	132	1	55	1.5785	16.3		16.3	48.1
			2	6	1.5590				
			3	3	1.5564				
	400	131	1	63	1.5779	15.3		15.3	50.8
			2	5	1.5646				
			3	1	1.5605				

On the basis of the refractometric data obtained, two curves were plotted (figures 1 and 2), showing the dependence of the index of refraction on the composition of the mixture expressed in per cent. By means of these curves the content of amines in the fractions was determined (with a certain approximation). When calculating we did not take into consideration the possible presence in every fraction of small amounts of a third component. Such an arbitrary supposition in the determination of the composition of the mixture leads to an error not exceeding 2 to 3 per cent. We used the refractometric curves in order to calculate for every experiment the percentage of the aniline transformed, so that the efficiency of different catalysts in the reaction of the ethylation of aniline could be compared.

The percentage of the aniline transformed is easily obtained, knowing the composition of the fractions and taking into account that for the formation of 1 g. of monoethylaniline and of diethylaniline, respectively, 93/121 and 93/149 g. of aniline are required.

The results obtained in all experiments are given in table 2. The loss of alcohol, due to decomposition, shown in the last column of the table, is calculated from the difference in weight between the initial mixture and the crude condensate, taking into consideration that the decomposition leads to the formation of ethylene.

DISCUSSION OF RESULTS

Comparing the results obtained, it may be seen that all the mixed catalysts that were tested in the reaction of the ethylation of aniline with alcohol proved to be less efficient compared with pure alumina.

Among the mixed catalysts investigated the most active ones in this process have been found to be $Al_2O_3 + Fe_2O_3$ and $Al_2O_3 + SnO$. As well as in the case of the ethylation of ammonia, the first of these catalysts, used at a temperature of 350 and 375°C., leads to a reaction with a smaller decomposition of alcohol as compared with pure alumina.

It is interesting to note that at a temperature of 400°C. the percentage of aniline transformed is in all cases and with all catalysts considerably smaller than at lower temperatures. In the case of pure Al_2O_3, $Al_2O_3 + NiO$, and $Al_2O_3 + ZnO$ it already attains its maximum value at 350°C.; in the case of other catalysts at 375°C.

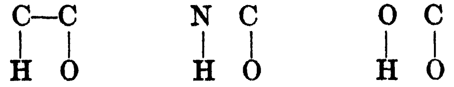
As a rule, the loss of alcohol due to decomposition increases with the rise of temperature; an exception is presented by $Al_2O_3 + ZnO$ at 375°C., but these results are within the limits of a possible error in the experiment. The loss of alcohol in the experiment with $Al_2O_3 + Cr_2O_3$ at 375°C. may be explained by a comparatively high yield of the products of the principal reaction of ethylation.

It should be noted that under the conditions of our experiments the mixed catalysts direct the reaction chiefly towards the formation of monoethylaniline. In the presence of pure alumina the relative yield of diethylaniline is considerably higher, which is shown by the determination of the composition of the condensates using the indices of refraction. Thus, for instance, in the case of pure alumina, at 400°C., about 42 per cent of aniline was transformed into monoethylaniline, and 7 per cent into diethylaniline, while at the same temperature, in the presence of Al_2O_3 + Fe_2O_3, about 39 per cent was transformed into monoethylaniline, and no transformation whatever into diethylaniline was observed.

An insufficient amount of alcohol in comparison with that required by theory for a complete transformation of aniline into diethylaniline (aniline: alcohol $= \sim 1:1.5$ instead of $1:2$) was taken with the purpose of promoting the formation of monoethylaniline. However, as the data of the present paper show, this measure was superfluous, as in the presence of the mixed catalysts that were used the secondary amine is formed almost exclusively.

It follows from all this, as well as from the consideration of the data of table 2, that in this case (as well as in the investigations concerning the ethylation of ammonia by alcohol) no additivity of the properties of oxides entering into the composition of mixed catalysts is observed.

The conclusions we have presented in our preceding paper concerning the specific properties of mixed catalysts when used for similar changes of the systems



$$\begin{array}{ccc} \begin{array}{cc} C\!-\!\!\!\!& C \\ | & | \\ H & O \end{array} & \qquad \begin{array}{cc} N & C \\ | & | \\ H & O \end{array} & \qquad \begin{array}{cc} O & C \\ | & | \\ H & O \end{array} \\ \text{II } K^2_{17}\ 3 & \qquad U(\text{I } K^2_1\ 1) & \qquad \text{II } K^3_{43}\ 1 \end{array}$$

differing only by the elements φ_{11} (C, N, and O, which change according to the order of their atomic numbers) remain also valid for the case being investigated, with the only difference that in the catalytic ethylation of aniline one must take into account the influence of the phenyl radical, which increases the rate of this reaction in comparison with a similar reaction, the ethylation of ammonia.

The addition to alumina of dehydrogenating oxides investigated by us causes the retardation of the reaction of class I K^2_1 1, contrary to the case of the hydrolysis of diethyl ether (class II K^3_{43} 1). This conclusion applies not only to the formation of monoethylaniline, but also to the retardation of the next stage—the formation of diethylaniline from monoethylaniline—a reaction, which, as one can easily see, requires the same index with the symbol U (I K^2_1 1).

Thus the application of mixed catalysts of the type investigated, decreasing the reaction rate, makes it possible to obtain synthetically monoalkylanilines, which are more difficult to obtain in a pure state than the dialkylsubstituted anilines (exhaustive alkylation).

CONCLUSIONS

1. In the present paper the action of mixed catalysts on the joint dehydration of aniline and ethyl alcohol has been studied; a dehydrating catalyst, alumina, was taken, to which oxides of metals promoting dehydrogenation were added.

2. The alkylating action of the catalysts studied after a single passing of the mixture of aniline with 96 per cent ethyl alcohol having a molecular ratio 1:1.45, at a rate of 12 cc. per hour, at 350, 375, and 400°C. may be seen from table 3.

TABLE 3

Alkylating action of the catalysts

CATALYSTS	TEMPERATURE CORRESPONDING TO A MAXIMUM TRANSFORMATION OF ANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	YIELD OF MONOMETHYLANILINE (RECKONED FROM ANILINE)	YIELD OF DIETHYLANILINE (RECKONED FROM ANILINE)
	°C	*per cent*		
Al_2O_3 . . .	350	67.5	64 3	3 2
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent) .	375	52 9	52 2	0 7
Al_2O_3 (90 per cent) + SnO (10 per cent)	375	50 2	48 7	1 5
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)...	375	43 2	43 2	Traces
Al_2O_3 (95 per cent) + NiO (5 per cent) .	350	38.5	38 4	0.1
Al_2O_3 (90 per cent) + ZnO (10 per cent) ...	350	31 6	31 6	Traces

3. It has been found that the above-mentioned additions decrease the reaction rate as compared with pure alumina.

4. This leads to the formation of monoethylaniline by preference, and this circumstance can be made use of for synthetic purposes.

5. The substitution of hydrogen by the phenyl radical in the molecule of ammonia increases the reaction rate of the joint dehydration with ethyl alcohol.

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THE ACTION OF HYDROGEN SULFIDE ON CHROMATES

Potassium Dichromate

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When a slow stream of hydrogen sulfide, purified by passing through scrubbers containing iodine and sodium sulfide, was passed into a 5 per cent solution of potassium dichromate of tested purity, the color of the solution first changed to a dark brown with the separation of a brown solid. As the current continued, the color changed to dirty brown and, passing through various shades, gave after four hours a whitish-green precipitate. When the color did not change perceptibly, the stream of hydrogen sulfide was stopped and the whitish green precipitate, which settled down, was filtered off. The filtrate was heated to coagulate colloidal chromium hydroxide and filtered. This filtrate was again subjected to the action of the gas but no more green precipitate separated, although there was a further deposit of sulfur.

The green precipitate consisted of chromium hydroxide, thiosulfate, and sulfur, and the filtrate contained thiosulfate and polysulfide of potassium. The observation (4) that sulfate is formed in the early stages of the reaction was due (while testing for sulfur acids) to the development of sulfate from tetrathionate, which is now shown to be an intermediate by-product of the reaction. The precipitate formed by the action of hydrogen sulfide on chromic acid (3) has been shown to contain sulfate also.

The mechanism of the reaction was studied by investigating the products at certain definite stages. Stage I, subsequently called the "intermediate stage": the gas was passed until the brown precipitate was just on the point of changing into green. Stage II—the final stage—when hydrogen sulfide was bubbled through the solution until precipitation was complete.

The intermediate stage

Hydrogen sulfide was passed into potassium dichromate solution (19–20°C.) with continual stirring for about half an hour until the green precipitate just began to form and the color of the reaction mixture was a dirty brown.

The reaction mixture was allowed to stand overnight in a stoppered flask and then filtered. An alkaline yellow filtrate was obtained, which contained potassium chromate and thiosulfate, but neither sulfide nor sulfate. Sulfate, in the presence of thiosulfate and chromate, was tested for by adding a 3 per cent solution of barium chloride to the alkaline filtrate in order to precipitate chromate and sulfate (if any). The washed precipitate was treated with dilute hydrochloric acid. The solid was completely dissolved, leaving no turbidity, showing the absence of sulfate, which is not formed if the concentration of hydroxyl ions is above a certain critical value.

The brown solid was insoluble in cold and hot water but dissolved in hydrochloric acid with evolution of sulfur dioxide and chlorine, giving a green solution containing free sulfur. Potassium was absent from the intermediate precipitate.

When treated with 0.3 *N* potassium hydroxide, a green solid remained which contained neither thiosulfate nor chromate. The alkali extract, however, contained both thiosulfate and chromate, showing that the coördinated complex was broken up by alkali treatment.

The molecular ratio of the chromium sesquioxide (Cr_2O_3) to chromic acid (CrO_3), calculated from chromate obtained by treatment of the brown solid with potassium hydroxide, was roughly constant. The mean of four determinations was $Cr:O_{1.93}$, which corresponds approximately to chromium dioxide (CrO_2) or chromium chromate ($Cr_2O_3 \cdot CrO_3$). Thus the brown solid is the same as that obtained by the action of hydrogen sulfide on chromic acid (3) and hence is different from the brown compound produced by the action of chromic acid on chromic sulfate.

Chromate in the presence of thiosulfate was estimated as follows: The alkaline liquid was carefully neutralized with dilute acetic acid, and the chromate precipitated with barium acetate from a boiling solution. After heating for some time to make the precipitate granular, it was filtered and washed in a sintered glass crucible, dried at 100–105°C., and weighed.

The brown product was thoroughly washed, suspended in water, and a current of hydrogen sulfide passed until a green precipitate was obtained. This was filtered off, washed, and found to contain sulfate.

The brown precipitate must be washed quite free from traces of both chromate and potassium, otherwise the reaction mixture develops alkalinity through the hydrolysis of KHS or K_2S_x, and no sulfate is formed. This shows that the oxidation of thiosulfate to sulfate does not take place in the presence of hydroxyl ions above a certain concentration.

The properties of the brown substance were compared with those of chromium dioxide, obtained by the action of sodium thiosulfate on potassium dichromate (9).

$$2K_2Cr_2O_7 + Na_2S_2O_3 \rightarrow K_2CrO_4 + K_2SO_4 + Na_2SO_3 + 3CrO_2 \qquad (1)$$

The solid was washed free from chromate, sulfite, and sulfate. It gave chlorine with hydrochloric acid, and chromate and chromium hydroxide with potassium hydroxide. The dark brown chromium dioxide was suspended in water and hydrogen sulfide passed until a green precipitate was obtained. This contained coördinated sulfate, chromium hydroxide, and sulfur. Thiosulfate was absent because the chromium dioxide contained no coprecipitated chromium hydroxide and sulfur (3).

The chromium dioxide in the precipitate from potassium dichromate was reduced in an alkaline medium and hence thiosulfate but no sulfate was formed.

TABLE 1

Examination of the products at the intermediate stage

Values are shown in mg. for 1 g of potassium dichromate

EXPERIMENT	TIME FOR WHICH ALLOWED TO STAND	FILTRATE		PRECIPITATE				TOTAL $K_2Cr_2O_7$ ACCOUNTED FOR	TOTAL THIOSULFATE
		*Unused $K_2Cr_2O_7$	Thiosulfate	*Unused $K_2Cr_2O_7$	Cr_2O_3 in the ppt	Corresponding $K_2Cr_2O_7$	Thiosulfate		
		mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
(a) .	Filtered immediately	313	58	79	303	586	11	978	69
(b). . . .	1 hour	316	56	75	309	598	13	989	69
(c). . . .	1 hour	295	54	72	319	616	12	983	69
(d). . .	4 hours	292	52	62	326	631	13	986	65
(e). . .	4 hours	300	59	68	326	631	15	984	74
(f). . . .	12 hours	304	63	65	319	618	14	987	77
(g). . . .	12 hours	312	68	67	318	615	14	995	82

* Calculated from chromate.

The following determinations were carried out at the intermediate stage (table 1): (1) The brown solid was extracted with potassium hydroxide (0.3 *N*) and the chromate and thiosulfate determined in solution. (2) The residual green solid was dissolved in hydrochloric acid and the chromium precipitated as hydroxide, which was weighed as Cr_2O_3. (3) Chromate and thiosulfate were also estimated in the filtrate, which does not contain any sulfide.

The lack of uniformity in the results is not surprising, as it is impossible to arrest the reaction at exactly the same point in each case. The values represent intermediate stages of a continuous reaction.

Experiments b and c, d and e, and f and g were carried out under exactly similar conditions and show that the reaction proceeds systematically.

Since the filtrate is alkaline and potassium hydroxide extracts chromate from chromium dioxide, one would expect that no sulfide of potassium is formed in the filtrate until all the chromium dioxide is removed from the solid phase. Careful investigation showed that, so long as chromate is present in the reaction mixture, potassium sulfide does not form. This was established by examining the action of hydrogen sulfide on potassium chromate, stopping the reaction at different stages, and testing for chromate and sulfide. As soon as chromate disappears from the liquid phase, sulfide makes its appearance.

The final stage

Hydrogen sulfide was passed until the precipitation was complete. On filtering, a whitish-green precipitate and a strongly alkaline, golden-yellow filtrate were obtained.

TABLE 2

The final green precipitate

EXPT. NO.	CONCENTRATION OF $K_2Cr_2O_7$ SOLUTION	AMOUNT TAKEN	Cr_2O_3	(S_2O_3) Iodometric method	(S_2O_3) $BaSO_4$ method	SULFUR FROM (S_2O_3)	TOTAL SULFUR	FREE SULFUR (BY DIFFERENCE)
	per cent	*cc.*	*grams*	*grams*	*grams*	*grams*	*grams*	*grams*
1	2	50	0.5144[a]	0.0212	0.0208	0.0059	0.0524	0.0475
2	2	50	0.5128	0.0214	0.0200	0.0061	0.0522	0.0461
3	3	50	0.7708[b]	0.0322	0.0316	0.0094	0.0781	0.0687
4	3	50	0.7712	0.0321	0.0312	0.0089	0.0766	0.0677
5	5	50	1.2892[c]	0.0532	0.0522	0.0150	0.1260	0.1110
6	5	50	1.2906	0.0529	0.0514	0.0142	0.1245	0.1103
7	5	50	1.2902	0.0531	0.0524	0.0149	0.1264	0.1115

Theory: a = 0.517 g.; b = 0.776 g.; c = 1.292 g.

The green solid was insoluble in water. With hydrochloric acid it gave sulfur dioxide and a green solution containing suspended sulfur. Thiosulfate was present, but neither sulfate nor polythionates. All the thiosulfate was extracted by treatment with potassium hydroxide and estimated in the filtered solution. The residue contained chromium hydroxide and free sulfur. The statement (4) that sulfate is produced in the reaction was especially investigated (see p. 1224) and found to be incorrect.

Sulfate is an important product in the action of hydrogen sulfide on chromic acid (3) and the fact that the final stage in the present case does not contain sulfate sets a limit to the oxidizing power of potassium dichromate. As already stated (p. 1218) the development of a considerable concentration of hydroxyl ions prevents the formation of sulfate in this case.

The strongly alkaline, final filtrate contained only thiosulfate and polysulfide of potassium.

Chromium hydroxide, thiosulfate, and free sulfur were estimated in the precipitate as described by Dunnicliff and Kotwani (3), in an attempt to define its composition (table 2).

Kurtenacker and Wollak's method (8) for the removal of sulfide in the presence of thiosulfate was also used, but it was observed that in the absence of sulfite the cadmium carbonate method gives accurate results.

Even when special precautions are taken (1), the free sulfur is invariably higher than theory, owing to dissolved oxygen in water, air contact, and, to some degree, the action of light.

The values for thiosulfate (column 5) obtained by titration agreed closely with those calculated from barium sulfate obtained by oxidation with bromine water. The latter value was not higher than the former in any instance, as would have been the case if a thionate had been present. The absence of a polythionate in the final stage was thus confirmed, and the only sulfur compound in the precipitate was thiosulfate. The existence of a trithionate was thus ruled out since, if formed, it should persist in the final stage (7), being the only thionate stable in the presence of hydrogen sulfide.

Coördinated and ionic thiosulfate

While trying to oxidize the sulfur and thiosulfate in the precipitate to sulfate with bromine water, it was observed that, even after refluxing for two hours, the remaining solid still contained thiosulfate. This slow attack of the thiosulfate by bromine suggested a method for distinguishing between ionic and coördinated thiosulfate groups in the complex molecule.

Portions of the precipitate were shaken with bromine water of various concentrations in the cold and filtered. The ratio A/B, between A, the thiosulfate estimated directly in the residue thus obtained, and B, that calculated from sulfate in the filtrate, shows very wide variations (table 3).

The inference is that bromine attacks both the ionic and coördinated thiosulfate. It is probable that, as the ionic thiosulfate is removed, the equilibrium between coördinated and ionic thiosulfate is disturbed and more ionic thiosulfate is formed. Possibly bromine is catalytic in this sense.

A series of experiments was tried using iodine. (1) The washed precipitates from a number of samples of 50 cc. of 5 per cent dichromate solution were treated with excess of different strengths of iodine solution and allowed to stand. The iodine disappeared entirely after times which increased with the strength of the solution. This was due to the adsorption of iodine by the solid particles. Hence methods involving excess of iodine solution were rejected. (2) After first making acid with dilute acetic acid, direct titrations with iodine of various strengths (0.1 *N* to 0.01 *N*) against a fine suspension were then performed (titer *a* cc.) in the hope that, when the ionic thiosulfate had all been attacked, a momentary end point might be obtained with starch used as an external indicator. After filtration, the precipitate was treated with potassium hydroxide and the acidified extract titrated against iodine (titer *b* cc.). It was found that $N/40$ to $N/60$ iodine gave $a/b = 2$ (approximately) (see table 4).

TABLE 3

Ionic and coördinated thiosulfate in the precipitate (bromine method)

TIME OF CONTACT	$BaSO_4$ FROM FILTRATE	A (S_2O_3) CALCULATED FROM $BaSO_4$	B (S_2O_3) IN THE PPT.	A/B
hours	*grams*	*grams*	*grams*	
1	0.0242	0.0058	0.0026	2.24
1	0.0366	0.0088	0.0051	1.17
1	0.0624	0.0149	0.0072	2.07
2	0.0532	0.0127	0.0040	3.17
2	0.0746	0.0179	0.0058	3.09
4	0.0382	0.0092	0.0024	3.83
4	0.0522	0.0125	0.0042	2.97
4	0.0388	0.0093	0.0038	2.46
12	0.0524	0.0125	0.0026	4.81
12	0.0692	0.0166	0.0031	5.35

TABLE 4

Titration of suspensions with iodine solutions

a	*b*	*a/b*	*a*	*b*	*a/b*	*a*	*b*	*a/b*
cc.	*cc.*		*cc.*	*cc*		*cc.*	*cc*	
2.30	1.05	2.19	1.95	0.90	2.17	2.85	1.30	2.19
3.80	1.70	2.23	2.10	1.15	1.83	3.20	1.55	2.07
2.30	1.20	1.92	2.60	1.20	2.17	2.45	1.05	2.33
2.45	1.15	2.15	2.50	1.25	2.00	1.80	0.85	2.11
2.60	1.10	2.36	3.30	1.55	2.13	2.30	1.05	2.19
Mean of 15 determinations = 2.14								

Considering the small titration volume and the presence of solid, which in any case adsorbs a little iodine, the agreement is significant and the ratio of the ionic to coördinated thiosulfate is probably of the order 2:1.

Composition of the final filtrate

Although the final filtrate is alkaline, it does not extract the whole of the thiosulfate from the precipitate as it does in the case of potassium chromate (4). Table 2 shows that the percentage of thiosulfate in the precipitate varies directly with the concentration of the solution used, and the constant values for experiments 1 and 2, 3 and 4, and 5, 6, 7 show that an equilibrium is set up between the thiosulfate (total) content of the precipitate and the concentration of thiosulfate in the solution.

After the removal of colloidal chromium hydroxide under reduced pressure the final alkaline filtrate contained only polysulfide and thiosulfate of potassium. The color varied between yellow and orange, with the amount of hydrogen sulfide passed and the temperature of the reaction. The whole of the potassium was in the filtrate. Potassium from 50 cc. of 5 per cent potassium dichromate: found 0.6605, 0.6614, 0.6612, and 0.6616 g.; theoretical value = 0.6633 g.

TABLE 5

Thiosulfate in filtrate (5 per cent solution of potassium dichromate)

g.S_2O_3 (by titration) × 10^4 (actual)	3321	3256	3241	3186	3146	3283	3132	3374	3125	3286
Calculated per 100 g. of $K_2Cr_2O_7$..	13 28	13 02	12 97	12 74	12 58	13 13	12 53	13 49	12 50	13.14

Mean = 12 93

TABLE 6

Values in grams per 100 grams of the polysulfide

NO.	(a) TOTAL POTASSIUM	(b) TOTAL SULFUR	(c) POTASSIUM THIOSULFATE $K_2S_2O_3$ $5H_2O$	(d) POTASSIUM PRESENT AS THIOSULFATE CALCULATED FROM (c)	(e) SULFUR PRESENT AS THIOSULFATE CALCULATED FROM (c)	(f) POTASSIUM PRESENT AS POLYSULFIDE (a) − (d)	(g) SULFUR PRESENT AS POLYSULFIDE (b) − (e)	CALCULATED FORMULA K_2S_y
	grams	*grams*	*grams*	*grams*	*grams*	*grams*	*grams*	
I	28 45	31 63	78.46	21 85	17 93	6 60	13.70	$K_2S_{5.06}$
II	27.72	29 60	84 35	23 50	19 30	4 22	10 30	$K_2S_{5.96}$
III	28 43	32 42	76 52	21 31	17 49	7 12	14 93	$K_2S_{5.12}$
IV	21 75	23 75	61 21	17 05	14 00	4 70	9 75	$K_2S_{5.08}$

Thiosulfate in the filtrate was estimated after removing the polysulfide by means of cadmium carbonate. The filtrate was acidified with dilute acetic acid and titrated against iodine. These values (table 5) varied slightly. Probably this was due to the conversion of some of the polysulfide into thiosulfate by contact with air (10). The determination had, therefore, always to be made in fresh filtrate.

When the reaction was allowed to proceed at the laboratory temperature (19–20°C.), the formula of the polysulfide worked out to K_2S_3 (mean of three determinations = $K_2S_{3.1}$).

In addition to the method of estimating the polysulfide sulfur given below, that of Kurtenacker and Bittner (6) was found to give satisfactory results, but the modified procedure of Szeberenyl (12) was found to be more convenient, as it avoids the necessity for tedious corrections.

In order to get the most polysulfide and to accelerate the otherwise slow reaction, hydrogen sulfide was passed into a 10 per cent solution of potassium dichromate at 80–85°C. for nearly ten hours. The chromium hydroxide which separated when the filtrate was concentrated under reduced pressure was filtered off, and the polysulfide allowed to crystallize out under reduced pressure at about 50°C. The crystals were pressed between folds of filter paper, keeping them, as far as possible, out of air contact. Potassium, "sulfide," and thiosulfate were determined in a weighed amount of the dried polysulfide (4).

Table 6 shows that the molecular ratio $K_2S_2O_3:K_2S_x$ is not constant. Possibly, under ideal conditions, potassium thiosulfate and pentasulfide are formed in equimolecular proportions.

With the exception of the potassium hydrosulfide, the analyses in tables 2 and 4 can be represented approximately by the following equation:

$$56(K_2Cr_2O_7 + 3H_2S + H_2O) \rightarrow Cr_2(S_2O_3)_3 + 110Cr(OH)_3 + 20(K_2S_2O_3 + KHS) + 26K_2S_3 + 24S + 49H_2O \quad (2)$$

Note on the observation (4) that sulfate is formed in the action of hydrogen sulfide on potassium dichromate

If the intermediate filtrate *is acidified* and then treated with barium chloride solution a white precipitate of barium sulfate is produced, but the final stage contains no sulfate. Since sulfate is not found in the final products and it is not decomposed by hydrogen sulfide, it is obvious that it was developed in testing, and the only source of such sulfate would be by the action of hydrochloric acid on a polythionate.

The reaction was studied in order to determine the exact stage at which the formation of sulfate *on acidification* is suppressed, i.e., when polythionate ceases to be a by-product, and the following procedure was adopted: A saturated solution of hydrogen sulfide was mixed in small but increasing quantities (10 cc. at a time) with 20 cc. of 5 per cent potassium dichromate and the products analyzed next day. The reaction was divided into three stages: (a) When up to 40 cc. of saturated hydrogen sulfide solution was added. A brown solid and a golden-yellow, slightly acidic filtrate were obtained. (b) On the addition of from 50 to 130 cc. of hydrogen sulfide solution, the precipitate was green and chromate was present in the filtrate. (c) When more than 130 cc. of hydrogen sulfide was added, the polysulfide made its appearance and the composition of the final precipitate (expt. 16, table 6) was almost the same as given in table 2, p. 1220.

Tables 7a, 7b, and 7c give results in which sulfate was precipitated by previous *acidification* and addition of barium chloride. The scheme for the analysis of all other radicals is as given previously.

The results show that (a) the amount of sulfate formed from 1 g. of potassium dichromate remains practically constant up to experiment 8; (b) so long as the solution is acidic, thiosulfate is not formed; (c) at a certain stage the sulfate entirely disappears, the disappearance being first apparent in the precipitate; and (d) so long as chromate is present in the filtrate or precipitate, a test for sulfate is given on acidification, but as soon as chromate disappears (expt. 12) the test for sulfate is negative.

TABLE 7a

Precipitates

Values are shown in mg. for 1 g. of potassium dichromate

(1) EXPT NO.	(2) COLOR OF PPT AND REACTION	(3) VOLUME OF H_2S USED	(4) CHROMATE IN TERMS OF $K_2Cr_2O_7$	(5) Cr_2O_3 IN PPT.	(6) CORRESPONDING $K_2Cr_2O_7$	(7) (SO_4) FROM THIONATE	(8) (S_2O_3)	(9) $K_2Cr_2O_7$ ACCOUNTED FOR IN PPT.
		cc	*mg.*	*mg*	*mg.*	*mg*	*mg*	*mg.*
1	Brown, acidic	30	62	120	233	14		295
2	Brown, acidic	40	64	158	306	14		370
3	Brown, neutral	50	62	302	584	11	13	646
4	Brown, alkaline	60	64	305	593	12	12	657
5	Dirty-brown, alkaline	70	22	342	663	4	13	685
6	Green, alkaline	80		352	681		12	681
7	Green, alkaline	90		359	695		16	695
8	Green, alkaline	100		351	679		12	679
9	Green, alkaline	110		363	699		11	699
10	Green, alkaline	120		478	925		14	925
11	Green, alkaline	130		491	950		16	950
12	Green, alkaline	140		513	993		16	993
13	Green, alkaline	150		516	999		16	999
14	Green, alkaline	160		514	995		16	995
15	Green, alkaline	170		512	990		18	990
16	Green, alkaline	180		514	995		18	995

The explanation is that sulfate is not present as such but is formed owing to the oxidation (by the chromic acid produced on acidification) of some thiosulfate or a thionate. Since, however, the values for thiosulfate show the same regular increase (expts. 11 and 12) without any abrupt change, the formation of sulfate is clearly due to the decomposition of a thionate.

TABLE 7b

*Filtrates**

(1) EXPT. NO.	(2) CHROMATE IN TERMS OF $K_2Cr_2O_7$	(3) $K_2Cr_2O_7$ CORRESPONDING TO COLLOIDAL $Cr(OH)_3$	(4) (SO_4) FROM THIONATE	(5) (S_2O_3)	(6) $K_2Cr_2O_7$ ACCOUNTED FOR IN THE FILTRATE
	mg.	*mg.*	*mg.*	*mg.*	*mg.*
1	625	54	59		679
2	578	22	61		600
3	306	21	62	58	327
4	299	18	61	59	317
5	292		59	60	292
6	293		61	55	293
7	290		69	61	290
8	294		73	68	294
9	266		19	70	266
10	49		19	83	49
11	15		8	94	15
12				98	
13				110	
14				117	
15				121	
16				121	

* The filtrates correspond to the precipitates in table 7a.

TABLE 7c

Total potassium dichromate accounted for and total sulfate and thiosulfate formed in precipitate and filtrate

EXPT. NO.	$K_2Cr_2O_7$ (TOTAL OF COLUMN 9 IN TABLE 7a AND COLUMN 6 IN TABLE 7b)	SULFATE (SO_4) (COLUMN 7 IN TABLE 7a AND COLUMN 4 IN TABLE 7b)	THIOSULFATE (S_2O_3) (COLUMN 8 IN TABLE 7a AND COLUMN 5 IN TABLE 7b)
	mg.	*mg.*	*mg.*
1	974	73	
2	970	75	
3	973	73	71
4	974	73	71
5	977	63	73
6	974	61	77
7	975	69	77
8	973	73	80
9	965	19	81
10	974	19	97
11	965	8	110
12	993		114
13	999		126
14	995		133
15	990		139
16	995		139

That sulfate is not a product of the reaction under consideration was shown as follows: The intermediate filtrate (and the alkali extract from the precipitate) were treated separately with barium chloride *without acidifying.* The precipitates were filtered. On treatment with hydrochloric acid the barium chromate dissolved out and no cloudiness or precipitate remained in solution. This was confirmed by determining sulfate by the old and new methods (see table 8).

Direct proof of the existence of a thionate

The alkaline filtrate from the intermediate stage was treated with barium chloride to remove chromate, and the filtrate made up to a known volume. An aliquot portion, after acidification with dilute acetic acid, was titrated against iodine. This gave the titer for thiosulfate existing normally in the filtrate.

TABLE 8

NO	VOLUME OF H_2S USED	WEIGHT OF $K_2Cr_2O_7$	$BaSO_4$ ON ACIDIFYING	$BaSO_4$ WITHOUT ACIDIFYING
	cc	*grams*	*grams*	*grams*
1	70	1 00	0 0875	0.0012
2	80	1 00	0 0768	0 0009
3	90	1 00	0 0764	0 0014
4	100	1 00	0 0787	0 0011

Another portion of the filtrate was treated with sodium sulfide; the white precipitate which formed was filtered off and the sulfide removed with cadmium carbonate. The filtrate from this when titrated with iodine gave a titer almost three times as large as that obtained before.

This is conclusive evidence of the existence of a thionate.

The existence of trithionate is ruled out since, if formed, it should persist in the final stages (7) (p. 1221). The polythionates which are possible under the existing conditions are the di- and tetra-thionates. Quantitative results show that a tetrathionate, which is easily converted into thiosulfate by an alkaline sulfide (11, 2), is present.

$$K_2S_4O_6 + Na_2S \rightarrow K_2S_2O_3 + Na_2S_2O_3 + S \qquad (4)$$

This would account for the fact that no potassium sulfide is present so long as tetrathionate exists. It also explains the regular increase in the thiosulfate content and the ultimate elimination of tetrathionate.

M. J. Fordos and A. Gellis (5) state that mild oxidizing agents like ferric chloride react with sodium thiosulfate to give tetrathionate.

$$2Na_2S_2O_3 + 2FeCl_3 \rightarrow Na_2S_4O_6 + 2NaCl + 2FeCl_2$$

Thus the tetrathionate is formed due to the oxidation of thiosulfate by the very weak chromic acid present in the initial stages. This reaction accounts for the fact that no test for tetrathionate is obtained when chromate is absent.

Direct estimation of tetrathionate was found to be cumbersome, and therefore the values for sulfate found by the acidification method have been given in tables 7a; 7b, and 7c.

SUMMARY AND DISCUSSION

The brown solid formed in the intermediate stages of the reduction of 5 per cent potassium dichromate by hydrogen sulfide consists of chromium dioxide and hydroxide, a coördinated chromium thiosulfate, chromium tetrathionate, and free sulfur, while the filtrate contains unattacked potassium dichromate together with potassium thiosulfate and tetrathionate.

The amount of tetrathionate decreases with the amount of chromate present, until eventually both disappear simultaneously.

So long as chromate remains sulfide is not present, and the dichromate accounted for as thiosulfate is less than theory by the amount of tetrathionate formed.

Accepting views previously advanced (3, 4) for the development of thiosulfate in these reactions, it has been shown that thiosulfate is the source of the tetrathionate formed in a side reaction, owing to the mild oxidation of part of the thiosulfate by chromate.

The tetrathionate is ultimately reduced to thiosulfate by the alkaline sulfide.

Sulfate is not formed in these reductions if the concentration of hydroxyl ions is above a certain critical value.

The final products are (a) a precipitate containing chromium hydroxide, sulfur, and a complex chromium thiosulfate in which the ratio of ionic to coördinated thiosulfate is approximately 2:1, and (b) potassium thiosulfate and polysulfide in solution.

The polysulfide formed depends on the temperature of the reaction, being K_2S_3 at laboratory temperatures and the pentasulfide at temperatures approaching 90°C.

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Editor's Note: Owing to unforeseen circumstances, the publication of this paper has been unavoidably delayed. A private communication from Professor Dunnicliff states that further investigation has proved that, if the reduction of sodium, potassium, or ammonium dichromates is carried out rapidly at 90–95°C., some sulfate appears in the product, but no sulfate is formed after the reaction mixture becomes alkaline. The formation of sulfate is totally suppressed in the alkaline media which result from the reduction of the chromates of sodium, potassium, and ammonium.

A study of the reduction of the insoluble chromates by hydrogen sulfide has also yielded valuable results. Among the reduction products of silver, mercurous, and thallous chromates at medium or low temperatures, sulfite has been found, while the chromates of lead, barium, strontium, etc. give no sulfite in any circumstances.

Evidence is adduced to show that sulfite is the precursor of both thiosulfate and sulfate in the general reaction. Details of this work will be published shortly.

PHOTOCHEMICAL REACTION BETWEEN SODIUM FORMATE AND IODINE AND A RELATION BETWEEN CHEMICAL REACTIVITY AND LIGHT ABSORPTION

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Amongst the photochemical reactions taking place in solutions, the iodine-formate reaction is easy to investigate as it is fairly rapid. N. R. Dhar (24) first showed that the reaction between sodium formate and iodine is markedly photosensitive; he studied the reaction only in visible light with iodine dissolved in an aqueous solution of potassium iodide, which considerably inhibits the reaction velocity. This reaction has now been investigated in detail, using an aqueous solution of iodine without any potassium iodide. In addition to kinetic measurements we have tried to establish a relation between chemical reactivity and light absorption photographically with different concentrations of the reactants.

EXPERIMENTAL PROCEDURE

A tilting-type quartz mercury-vapor lamp working at 220 volts was used in order to obtain ultra-violet radiations, whereas for visible and infra-red radiations, a 1000-watt gas-filled tungsten filament lamp was employed. All materials used were purified by recrystallization. Merck's pure iodine was further purified by resublimation. All solutions were prepared in conductivity water. In order to isolate different regions from the entire spectrum of the light source, solution filters were used. The light transmitted by these filters has been carefully determined and described in previous papers (1). The filters used for infra-red radiations cut off all the visible and ultra-violet light. For measurements of the energy absorbed, a Moll thermopile with a sensitive galvanometer was used. The velocity of the reaction at a particular instant was ascertained by estimating the unchanged iodine against very dilute solutions of sodium thiosulfate.

The reaction is monomolecular in the dark. The expression for a semimolecular reaction velocity is

$$K_{\frac{1}{2}} = \frac{2}{t}\left\{\frac{1}{\sqrt{a - x}} - \frac{1}{\sqrt{a}}\right\}$$

where a denotes the initial concentration of the reactant and x its concentration after a period t. The reaction between sodium formate and iodine follows the semimolecular law when the system is illuminated by radiations of different wave lengths, as is clear from table 1.

KINETICS

The temperature coefficients have been calculated after deducting the dark reaction velocity (see tables 2 and 3).

The results show that Einstein's law of photochemical equivalence is not obeyed. This is true for many exothermal photochemical reactions, and it appears that the energy given out in the transformation of molecules, caused by light absorption, may effect activation or loosening of the binding forces of molecules. The quantum yield increases with temperature and the frequency of the incident radiation.

TABLE 1

The reaction between sodium formate and iodine

CONDITIONS	TIME	HYPO PER 5 CC. OF THE REACTING MIXTURE	REACTION VELOCITY
	minutes	*cc.*	
Dark (T = 20°C.)	0 10 20	4.6 3.75 3.05	0.00888 (K_1) 0 00892 (K_1)
Mean K_1			0.00890
λ = 4295 A.U. (T = 15°C)	0 10 20	4.6 3.7 2.9	0.04419 ($K_{\frac{1}{2}}$) 0.04416 ($K_{\frac{1}{2}}$)
Mean $K_{\frac{1}{2}}$			0.04418

RELATION BETWEEN THE INTENSITY OF LIGHT (AMOUNT OF ENERGY ABSORBED) AND THE VELOCITY OF REACTION

We have investigated the problem of the variation of the relation between intensity and velocity by changing the amounts of potassium iodide (a marked retarder) present in the iodine solution, and thus altering the dark reaction velocity. The results given in table 4 show that the relation between the velocity and intensity in the reaction between sodium formate and iodine at 20°C. can vary from $I^{\frac{1}{2}}$ to $I^{\frac{1}{4}}$.

From the results given in table 4 it is obvious that there are two important factors which are of consequence in the relation between intensity and velocity of the reaction: (1) the amount of absorption of the incident radiation by the reacting system, and (2) the acceleration of the reaction on illumination. A photochemical reaction which follows less than direct relationship, becomes directly proportional or even greater than proportional to the intensity of incident radiation, by increasing the dark reaction velocity and exposing it to radiation, slightly absorbed by the system. On

TABLE 2

Reaction between sodium formate and iodine (aqueous without potassium iodide)
$N/25$ sodium formate; $N/1125$ iodine; $N/400$ borax (used as buffer)

CONDITIONS	TEMPERATURE	K (SEMIMOLECULAR)	TEMPERATURE COEFFICIENTS	QUANTUM YIELD
	°C			
Dark	15	0.03393		
	20	0.04166	1.77	
	25	0.06012		
λ = 3125 A.U. (range of transmission = 3290–2961 A.U.)	15	0.06101		32
	20	0.07214	1.45	46
	25	0.09921		64
λ = 3340 A.U. (range of transmission = 4063–2618 A.U.	15	0.05282		31
	20	0.06485	1.52	40
	25	0.08835		54
λ = 3452 A.U. (range of transmission = 3307–3598 A.U.)	15	0.04865		26
	20	0.06120	1.57	36
	25	0.08329		42
λ = 3512 A.U. (range of transmission = 3290–2961 A.U., 4023–4063 A.U.)	15	0.04865		
	20	0.06120	1.57	
	25	0.08329		
λ = 4295 A.U. (per cent of transmission = 20.4; range of transmission = 4000–4590 A.U.)	15	0.04418		
	20	0.05688	1.61	
	25	0.07669		
λ = 5700 A.U. (per cent of transmission = 16.2; range of transmission = 5200–6200 A.U.)	15	0.04059		
	20	0.05187	1.66	
	25	0.07119		
λ = 6640 A.U. (per cent of transmission = 58.8; range of transmission = 6280–7000 A.U.)	15	0.03859		
	20	0.04696	1.71	
	25	0.06809		
λ = 8500 A.U. (range of transmission = 8000–9000 A.U.)	15	0.03662		
	20	0.04417	1.75	
	25	0.06483		

the contrary, a photochemical reaction which is nearly proportional to the square of the incident radiation or is directly proportional can be made to be proportional to the square root of the incident radiation by decreasing the dark reaction velocity. This is certainly one of the many reactions which have been proved by us to show a variable relation between the velocity and the light intensity or amount of energy absorbed (compare reference 4, pp. 340–4).

TABLE 3

Reaction between sodium formate and iodine (aqueous solution containing a little potassium iodide)

N/6.25 sodium formate; *N*/6.7 sodium acetate; *N*/204 iodine; *N*/47.4 potassium iodide

CONDITION	TEMPERATURE °C.	$K_{\frac{1}{2}}$ (SEMI-MOLECULAR	TEMPERATURE COEFFICIENTS
Dark	20	0.00883	4.26
	30	0.03760	4.17
	40	0.15686	
λ = 4295 A.U	20	0.01216	3.95
	30	0.05076	3 84
	40	0 20736	
λ = 5700 A.U	20	0.01104	4.14
	30	0 04676	4.04
	40	0.19391	
λ = 6640 A.U	20	0.010529	4.19
	30	0.04472	4.02
	40	0 18547	
λ = 8500 A.U	20	0.00928	4.22
	30	0.03948	4.12
	40	0.16461	

Temperature coefficients

The results recorded in table 2 show that the temperature coefficient of the dark reaction velocity has the value 1.77 between 15°C. and 25°C., when aqueous solutions of iodine are employed. On the contrary the temperature coefficient has the value 4.26 between 20°C. and 30°C., and 4.17 between 30°C. and 40°C., when a little potassium iodide (*N*/47.4) is added to the aqueous iodine solution. Potassium iodide markedly retards the reaction. This is in agreement with the observations of N. R. Dhar (3), who showed that the temperature coefficient of a reaction falls off when

TABLE 4

Relation between reaction velocity and light intensity

EXPT.	REACTANTS	SOURCE OF LIGHT	DIAMETER OF THE APERTURE IN CM	DARK REACTION VELOCITY	K_1 (MONOMOLECULAR AFTER DEDUCTING THE DARK REACTION VELOCITY
A	N/6.25 sodium formate; N/6.7 sodium acetate; N/204 iodine; KI, 1.0464 g. in one liter	Total light from 1000-watt lamp	2.2 0.5 1.0	0.00561	0.00566 I 0.00035 III 0.001293 II
B	N/6.25 sodium formate; N/6.7 sodium acetate (as buffer); N/204 iodine; N/47.4 potassium iodide	Total light from 1000-watt lamp	2.2 1.0 0.5	0.00180	0.00472 I 0.00132 II 0.00044 III
C	N/25 sodium formate; N/1125 iodine without KI; N/26.8 sodium acetate	Total light from 1000-watt lamp	2.2 1.0 0.5	0.00826	0.00764 I 0.00166 II 0.00060 III
D	N/25 sodium formate; N/1125 iodine; N/400 borax (as buffer)	Total light from 1000-watt lamp	2.2 1.0	0.00890	0.00483 I 0.00091 II
E	Same as in D	Mercury vapor lamp, λ = 3340 A.U.	2.2 1.0		0.01954 I 0.00288 II
F	Same as in D	λ = 3125 A.U.	2.2 1.0		0.02083 I 0.00372 II

EXPT.	RATIO OF VELOCITIES	IF DIRECTLY PROPORTIONAL TO CHANGE IN INTENSITY	EXPT	RATIO OF VELOCITIES	IF DIRECTLY PROPORTIONAL TO CHANGE IN INTENSITY
A	I/II = 4.37 II/III = 3.67 I/III = 16.07	4.84 4.0 19.36	C	I/II = 4.6 II/III = 3.8 I/III = 17.5	4.84 4.0 19.36
B	I/II = 3.57 II/III = 3.0 I/III = 10.7	4.84 4.0 19.36	D	I/II = 5.3	4.84
			E	I/II = 6.7	4.84
			F	I/II = 5.6	4.84

it is accelerated and rises when it is retarded. Moreover, it will be observed that the temperature coefficient in ultra-violet light, which markedly accelerates the reaction, varies from 1.45 to 1.57 between 15°C. and 25°C. Hence it is clear that the greater the velocity of the reaction in light, the smaller is the temperature coefficient of the reaction.

When the reaction is accelerated by infra-red radiations of mean wave length 8500 A.U., which affect the velocity much less than ultra-violet light, the difference between the temperature coefficients of the thermal and photochemical velocities is much less. In radiations of wave length 8500 A.U. the temperature coefficient between 25°C. and 15°C. is 1.75. In other words, the greater the acceleration of the reaction by light absorption, the smaller is the temperature coefficient.

CHEMICAL REACTIVITY AND LIGHT ABSORPTION

We have measured the light absorption of the reacting substances separately and in mixtures by photographing their absorption spectra with Hilger quartz spectrographs E_1 and E_3 using a copper arc as the light source. The effect of increase in the concentration of sodium formate on light absorption on the entire spectrum, with a constant concentration of iodine and *vice versa*, has also been investigated photographically. The exposure for taking the photographs was varied from 7 to 45 seconds. The amount of chemical change during the period of exposure was negligible, and hence the products formed as a result of the chemical change from the reacting mixtures did not play any important part in effecting the light absorption. We have tested this by taking the photographs with 20

FIG. 1. VISIBLE AND ULTRA-VIOLET REGION

From 5220 to 3247 A.U. Exposure = 45 seconds. Illford rapid plates

	Light absorption
(1) Copper arc	
(2) *N*/700 iodine	5220–5105 A.U. 5105–4580 A.U. 4573–4441 A.U. 3577–3426 A.U. 3426–3282 A.U.
(3) *N*/2 sodium formate	No absorption
(4) Mixture of *N*/350 iodine with *N* sodium formate	5220–5105 A.U. 5105–3247 A.U.
(5) *N*/4 sodium formate	No absorption
(6) Mixture of *N*/2 sodium formate with *N*/350 iodine	5105–4850 A.U. 4441–3247 A.U.
(7) *N*/8 sodium formate	No absorption
(8) Mixture of *N*/4 sodium formate with *N*/350 iodine	5105–4441 A.U. 4441–3266 A.U.
(9) *N*/12.5 sodium formate	No absorption
(10) Mixture of *N*/6.25 sodium formate with *N*/350 iodine	5105–4441 A.U. 4441–3266 A.U.

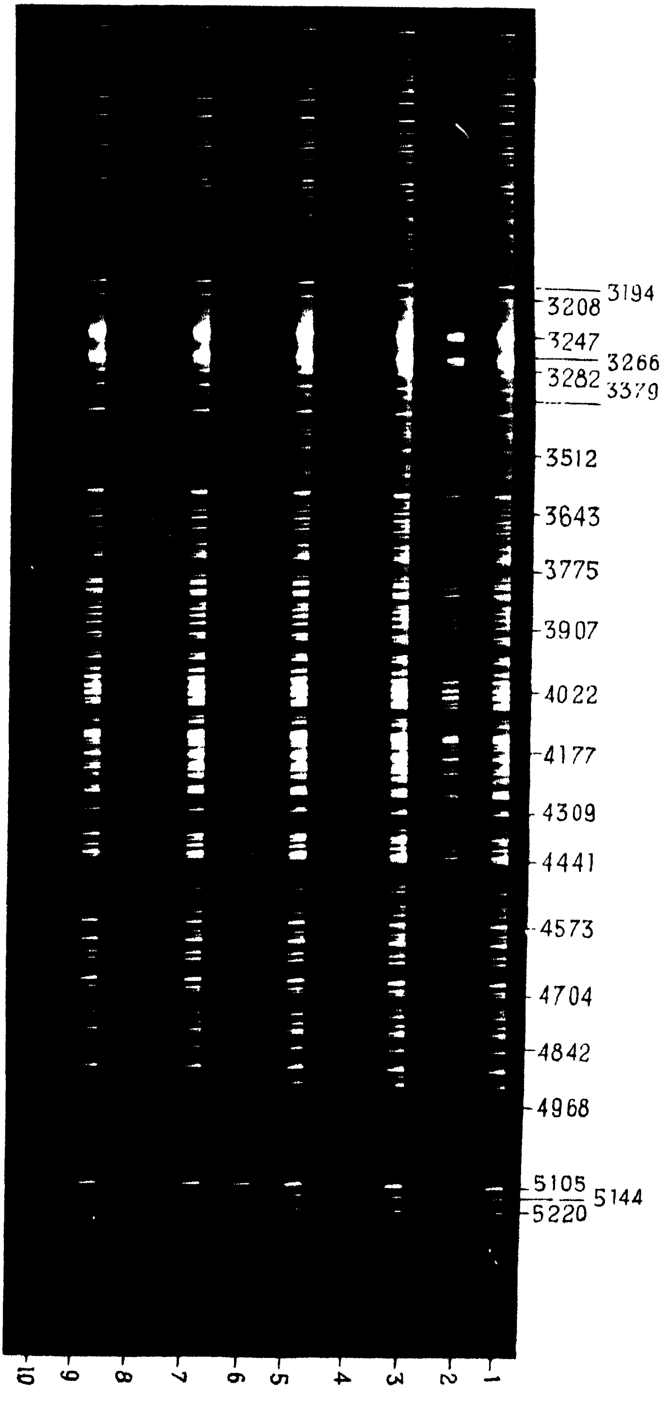
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FIG. 1

seconds and 7 seconds exposure and found no perceptible difference in light absorption.

Figures 1 to 5 are the photographs taken with different concentrations of sodium formate and a constant concentration of iodine (aqueous), separately and with mixtures.

From the photograph taken with $N/2$ sodium formate and $N/700$ iodine separately and their mixtures, it is evident that the iodine solution alone shows complete absorption from 2369 A.U., while with sodium formate complete absorption begins from 2294 A.U., but in the mixture complete absorption starts from 5216 A.U. It appears, therefore, that the presence of sodium formate sensitizes the decomposition of iodine molecules, which becomes reactive in radiations of longer wave lengths on the addition of sodium formate. The addition of sodium formate weakens the binding forces of halogen molecules, which are readily broken up either by increase of temperature or illumination, and thus increased light absorption has been observed with the mixture. Hence the reactivity of a mixture is preceded by the formation of an additive product with the weakening of the binding forces and increased light absorption.

Our experimental observations further show that the increase in the concentration of the reducing agent leads to more light absorption by the mixture. In other words, the higher the concentration of the reducing agent, the greater is the light absorption by the mixture of the reducing agents with the halogens. This may be due to the loosening of the binding forces of more of the iodine molecules, leading to increase in light absorption, especially of *visible and ultra-violet regions.*

It has also been observed by us that the decrease in the concentration of iodine, keeping the concentration of sodium formate constant, leads to a diminution of light absorption by the mixture, as is clear from the above photographs. It is interesting to note that the variation of the concentration of iodine produces more marked effect on light absorption by the mixture than when the concentration of the reducing agent is altered.

FIG. 2. VISIBLE AND ULTRA-VIOLET REGION

From 5220 to 3274 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc	
(2) $N/1400$ iodine .	5105 4573 A.U
	4573 4441 A U.
(3) $N/2$ sodium formate .	No absorption
(4) Mixture of N sodium formate and $N/700$ iodine	4022 3266 A.U.
(5) $N/4$ sodium formate . .	No absorption
(6) Mixture of $N/2$ sodium formate and $N/700$ iodine	3907-3379 A.U.
(7) $N/8$ sodium formate	No absorption
(8) Mixture of $N/4$ sodium formate and $N/700$ iodine...	3775–3400 A.U.

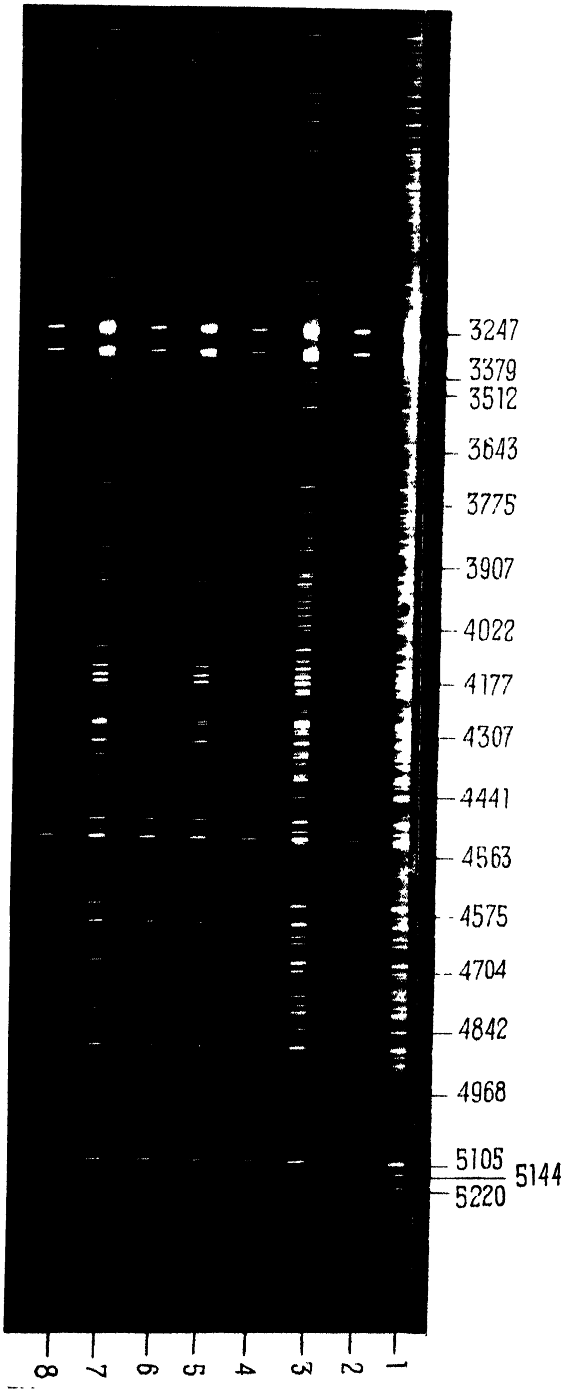
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Fig. 2

The observations of Fajans and Karagunis (5) on increased light absorption by silver halides containing adsorbed silver and those of Weigert and Kellermann (7) on increased light absorption by a mixture of chlorine and hydrogen, and the increased light absorption observed by J. C. Ghosh and collaborators (6) with mixtures of organic substances and solutions of ferric and mercuric chlorides and uranyl nitrate, etc., can be interpreted on the viewpoint that the chemical reactivity of these various systems is associated with the weakening of the binding forces and increased light absorption.

Our conclusions are also supported by the observations of Franck and Victor Henri, who showed that light absorption or increased temperature enhances the reactivity and the power to absorb light of gaseous molecules. Just as the physical agencies like light absorption, increase of temperature, etc., can loosen the binding forces of the molecule, so the introduction of a reactive chemical substance into a light-absorbing system can weaken the

FIG. 3. ULTRA-VIOLET REGION
From 3247 to 2442 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc . . .	
(2) $N/700$ iodine .	3000 2961 A.U. 2961 2824 A.U. 2824- 2766 A U. 2766-2618 A.U. 2600-2492 A.U. 2492-2442 A.U.
(3) $N/2$ sodium formate	No absorption
(4) Mixture of N sodium formate and $N/350$ iodine	Total absorption
(5) $N/1400$ iodine .	2961 2882 A.U. 2880 2824 A.U. 2824- 2766 A.U. 2729-2618 A.U.
(6) $N/4$ sodium formate	No absorption
(7) Mixture of $N/2$ sodium formate and $N/350$ iodine	Total absorption
(8) Mixture of $N/2$ sodium formate and $N/700$ iodine	3194-2618 A.U. 2618 onwards total
(9) $N/8$ sodium formate . .	No absorption
(10) Mixture of $N/1$ sodium formate and $N/350$ iodine . .	3247 2618 A.U. 2618 onwards complete
(11) Mixture of $N/4$ sodium formate and $N/700$ iodine . . .	3012-2618 A.U. 2610-2492 A.U. 2492 onwards complete

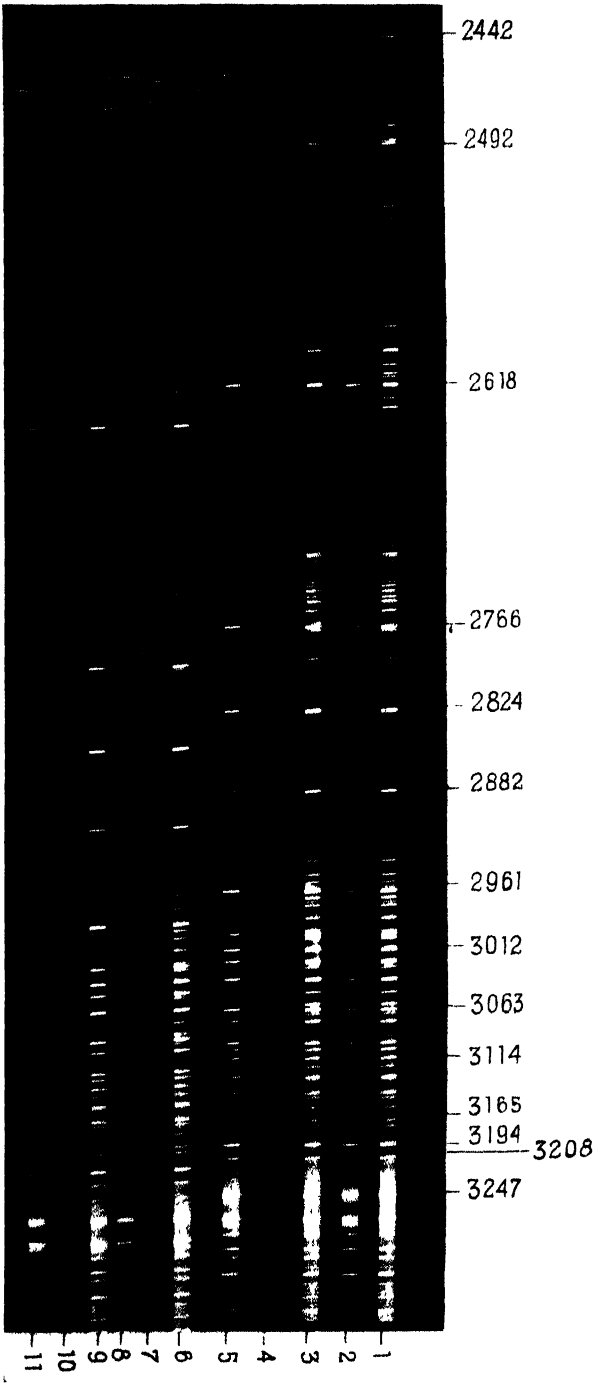
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FIG. 3

FIGS. 4 AND 5. ULTRA-VIOLET REGION

From 2406 to 2104 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc	
(2) $N/700$ iodine	2406–2398 A.U. 2398 2392 A.U. 2392 2369 A.U. and onwards complete
(3) $N/2$ sodium formate	2369 onwards complete
(4) Mixture of $N/350$ iodine and N sodium formate	Total absorption
(5) $N/4$ sodium formate	From 2369 total absorption
(6) Mixture of $N/2$ sodium formate and $N/350$ iodine	Total absorption
(7) Copper arc	
(8) $N/1400$ iodine	2369 A.U onwards complete absorption
(9) Mixture $N/700$ iodine and N sodium formate	Total absorption
(10) Mixture $N/700$ iodine and $N/2$ sodium formate.	Total absorption
(11) $N/8$ sodium formate	2369 2303 A.U. 2303 onwards complete absorption
(12) $N/4$ sodium formate and $N/350$ iodine	Total absorption
(13) $N/4$ sodium formate and $N/700$ iodine	Total absorption

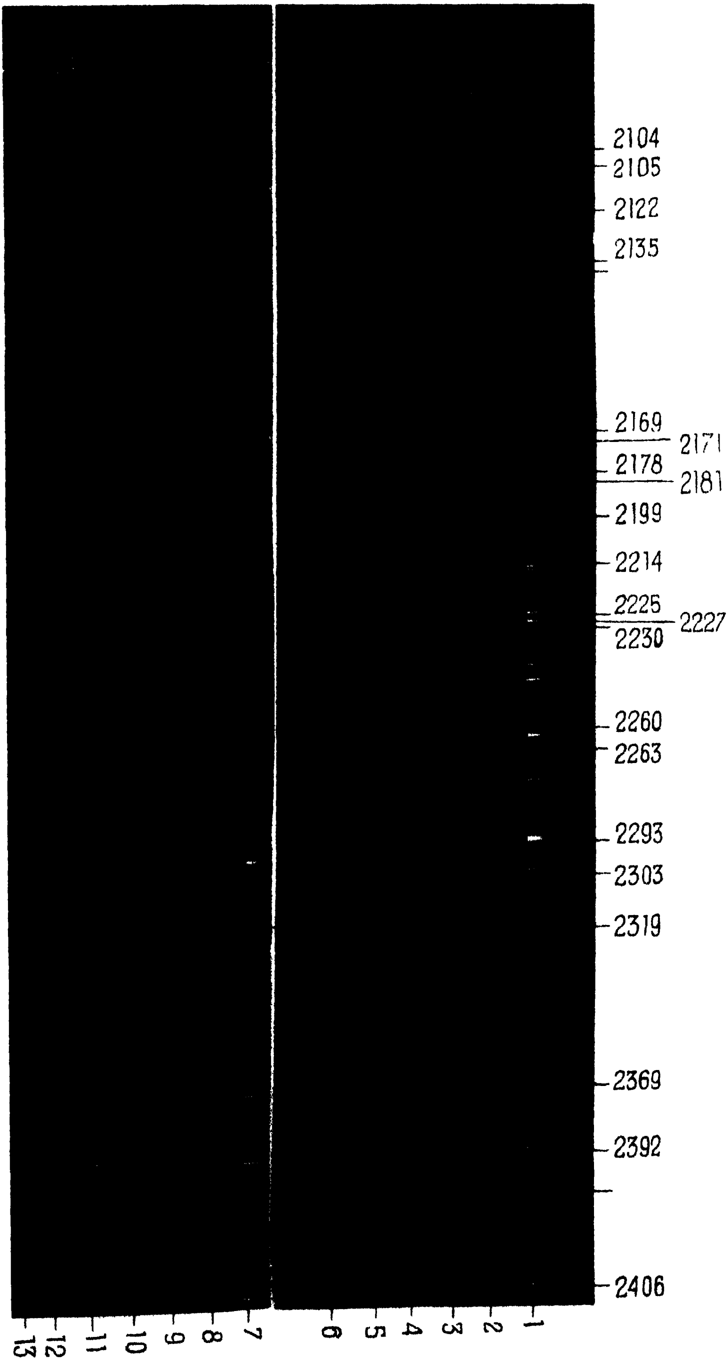
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Fig. 4 and 5

binding forces of the molecule. In other words, the presence of a reducing agent like sodium formate sensitizes the decomposition of iodine molecules and makes them reactive in radiations of longer wave lengths. It seems that chemical reactivity is associated with increased light absorption.

SUMMARY

1. The reaction between sodium formate and iodine (aqueous) in the absence of potassium iodide is unimolecular in the dark and semimolecular in light.

2. The temperature coefficient of the reaction velocity between 15°C. and 25°C. has the following values: 1.77 (dark), 1.75 (8500 A.U.), 1.71 (6640 A.U.), 1.66 (5700 A.U.), 1.61 (4295 A.U.), 1.57 (3512 A.U.), 1.57 (3452 A.U.), 1.52 (3340 A.U.), and 1.45 (3125 A.U.). The greater the acceleration due to light, the smaller is the temperature coefficient.

3. The relation between light intensity and velocity of the reaction varies from $I^{\frac{1}{4}}$ to $I^{\frac{1}{2}}$.

4. Einstein's law of photochemical equivalence is not obeyed. The quantum yield increases with the temperature and the frequency of the incident radiation.

5. It has been observed that the light absorption by a mixture of sodium formate and iodine is greater than the absorption by the ingredients. The increased absorption appears to be due to the activation of the iodine molecules by the presence of the molecules of the reducing agent. The activation of the molecules is associated with the weakening of the binding forces and consequent increased light absorption.

The increase in the concentration of sodium formate or iodine causes an increase in the light absorption by the mixture of sodium formate and iodine.

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THE ABSORPTION OF CAUSTIC SODA BY CELLULOSE

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Received June 6, 1935

In a recent paper by Bancroft and Calkin (1) highly accurate data for the composition of the liquor removed by centrifuging a mass of cellulose impregnated with caustic soda solution are given. These authors make use of the change in concentration of the centrifuged liquor to determine the point where "adsorbed solution" begins to come off, and so to calculate the "true" adsorption as distinct from the "apparent" adsorption calculated from the change-in-titer method. They do not emphasize, however, the importance of the fact that the concentration of the adsorbed solution removed by powerful centrifuging falls steadily as centrifuging proceeds. There appears to be no *a priori* reason why this should be the case, but it would follow if the concentration of free hydroxyl ion in the adsorbed solution is determined by the Donnan equation, as suggested by the author (2).

The following values derived from the latter half of table 1 of Bancroft and Calkin's paper demonstrate that this fall is very marked.

CENTRIFUGING TIME INTERVAL	GRAMS REMOVED IN INTERVAL		"INTERVAL" CENTRIFUGED LIQUID NaOH PER GRAM OF H_2O
	NaOH	H_2O	
minutes	*grams*	*grams*	*grams*
0–$\frac{1}{4}$	0.1573	0.831	0.1893
$\frac{1}{4}$–$\frac{1}{2}$	0.0120	0.070	0.171
$\frac{1}{2}$–1	0.0143	0.086	0.166
1–3	0.0064	0 050	0.128

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NEW BOOKS

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Annual Tables of Constants. A.C. and Numerical Data Chemical, Physical, Biological and Technological, published under the patronage of the International Union of Chemistry. Volume X. Two parts, about 1800 pages. New York: McGraw-Hill Book Co., Inc., 1930. Price (for subscribers): cloth, $20.00.

This very useful volume covers the research published in 1930. All texts are given in both French and English.

F. H. MacDougall.

Hochpolymere organische Naturstoffe. By H. Saechtling. 22 x 14 cm.; vi + 125 pp. Braunschweig: Friedr. Vieweg und Sohn, 1935. Price: 8 RM.

This is a neat little book, just the thing one wants nowadays when it is fast becoming almost impossible to attend to one's business and at the same time take an intelligent interest in, let alone make proper use of, other people's work. The structure and properties of the high polymers and condensation products, natural and artificial, is a big subject which daily grows more and more important both for biology and industry, but the gist of it is well set out here, and the author is to be congratulated on his contribution. There are several other, and larger, books available, each authoritative in its way, but Dr. Saechtling has tried to dissociate himself from any particular viewpoint or method of approach, and has concerned himself rather with bringing out as concisely as possible the essential unity of ideas that has now been reached.

After a statement of the problem, the treatment falls into seven chapters, dealing in turn with the general chemical principles underlying the structure of the natural high polymers, microscopic investigations, x-ray investigations, constitutional chemistry, structure and mechanical properties, artificial high polymers as an aid to understanding the natural high polymers, and natural growth structures, the whole being supported by a selection of more specialized textbooks and a list of no fewer than 239 references to original papers. For the most part the argument rests, of course, on cellulose, the proteins, and rubber, but it will be seen that the scheme is eminently reasonable, and there can be no hesitation about recommending this book to anyone looking for a rapid and up-to-date sketch of a field that is not merely of great technical significance but that lies at the very foundation of the science of life itself.

W. T. Astbury.

Molekülspektren und ihre Anwendung auf chemische Probleme. I. Tabellen. By H. Sponer. 21 x 14 cm.; vi + 154 pp. Berlin: Springer, 1935. Price: unbound, 16 RM; bound, 17.60 RM.

Customarily tables of data such as these would form an appendix to the main text of a comprehensive work. The plan here adopted of issuing the tables separately has the double advantage of enabling the author to revise the tables more frequently than the text and readers who so wish to have the tables without the text, which is to follow in volume II. The tables for diatomic molecules contain constants for all the known electronic states and band systems, observed isotope effects, predissociations, alternating intensities and nuclear spins, and electron impact processes. Most of them are based, as Dr. Sponer very generously acknowledges, on the corresponding tables in the reviewer's Report (Physical Society, 1932), supplemented by more recent data and by columns giving electron configurations and dissociation products. For polyatomic molecules the tables, which are entirely new, cover infra-red and Raman spectra (with diagrams showing modes of vibration), electronic bands, and electron impact processes. Data published while the rest of the volume was in the press in 1934 and early 1935 are included in two supplementary tables. A brief explanation and a list of references accompany each group of tables, and the work is well indexed. Remarkably few omissions and numerical errors have been detected. The compilation, which represents a vast amount of careful work, will be invaluable to spectroscopists and chemists.

W. JEVONS.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 53: Molybdän. 25.5 x 17.5 cm.: xi + 393 pp. Verlag Chemie, 1935. Price: 64 marks.

The present volume deals with the ores of molybdenum, the extraction, refining, and physical and chemical properties of the metal and its alloys, and with the chemistry of the compounds of molybdenum, including the heteropolyacids. The treatment is very detailed and physicochemical aspects are well represented. The book contains a wealth of accurate and well-arranged information, and the literature is covered till the end of 1934.

J. R. PARTINGTON.

Kristallplastizität. By E. SCHMID and W. BOAS. 22 x 15 cm.; x + 373 pp. Berlin: Julius Springer, 1935. Price: 32 marks (paper covers), or 33.80 marks (bound).

The study of crystal plasticity has made remarkable progress in recent years; this has been achieved by a number of workers largely independent of each other, and not infrequently approaching the problem with different aims. For example, the plastic nature of the crystalline state is of great importance to the engineer in his search for special alloys; the chemist and physicist, however, are more concerned to extract what they can to shed light upon the nature of the forces acting in the lattice. The authors of the present book have in fact provided an encyclopaedia of all that is at present known about these matters, with special reference to metals.

The volume falls into three parts,—general, special experimental results, and the significance of the effects shown by single crystals. An idea of the scope embraced by the writers can be gathered from the list of references collected at the end, which number over seven hundred entries.

The discussion of hardness in ionic crystals is exceptionally clear. Two points are stressed (which even to-day need underlining), firstly that hardness is not a definite quantity, but only has a meaning when expressed in terms of a particular method of determination, and secondly, that the time is not yet when we can link such observations with crystal strength, and consequently, no doubt, with lattice properties. Scratch-hardness curves for rock salt and fluorite on the (100) and (111) faces are delightful illustrations of the anisotropy of a surface. The same is true of the pendulum method for rock salt on (001), yielding maximum values of about 0.5 with an intervening minimum as low as about 0.2.

The price of the book is very high, but for those wishing to have all the information there is to be had about plasticity in crystals, this book should be invaluable. As in the case of other Springer publications, the format is excellent.

F. I. G. RAWLINS.

The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases. By J. T. **Randall.** 23 x 15 cm.; xii + 290 pp. London: Chapman and Hall, 1934. Price: 21s.

In producing this book Dr. Randall has done a great service to science. Ever since the discovery, in 1912, of diffraction of x-rays by crystals our knowledge of the solid state has gone forward by leaps and bounds. And now, Dr. Randall produces a volume covering the field of diffraction of rays in non-crystalline media. His treatment is admirably logical. He begins with a short summary of the methods of crystal analysis by x-rays and electrons. This introduces the fundamental notion of the diffraction pattern of a crystal consisting of rays of different intensities and the effect on this pattern of decreasing the size of the crystal, as in this way is reached the liquid state, being the limit of infinite diminution of crystal size. Before passing to liquids, however, it is necessary to see what the diffraction effects of individual atoms and molecules are, and this can be determined by the diffraction of electrons and of x-rays in gases where the mutual diffraction of molecules is neglected. A description is given of modern methods of electron molecular analysis. The diffraction of liquids represents the superposition of effects of the individual molecules and their mutual position.

Dr. Randall gives particular attention to the structure of liquid metals, water, and the paraffins. He proceeds from the study of liquids to the consideration of the glasses and gives a careful description of the phenomenon of vitrification.

The remaining chapters are devoted to a discussion of fibers, the structure of surfaces as revealed by electron diffraction, and finally the nature of liquid crystals.

The treatment throughout is admirably clear. There is a full bibliography. The whole of the subject is still in a controversial state, but Dr. Randall is fair and reserved in his conclusions. Anyone who has read this book will have acquired a knowledge of the structure of liquids and glasses which is bound to be of great value in dealing with both the chemical and physical sciences.

J. D. **Bernal.**

Principles of Phase Diagrams. By J. S. **Marsh.** 193 pp. New York: The McGraw-Hill Book Company.

This excellent work purports to provide a "moderately strong grounding in the principles of the phase theory," but it does considerably more than that. It furnishes a skeleton for the study or review of a generous slice of the field of fundamental thermodynamics. It is by no means a book that can be skimmed, as the reviewer soon discovered. In the foreword Dr. John Johnston warns that it is not for the casual reader and "even the studious reader will find that he must himself do a deal of hard thinking."

The book apparently evolved away from the original idea. It is one of the Alloys of Iron Research Series and was originally intended as a utilitarian key to point the way to interpretation of some of the numerous phase diagrams with which metallographists and metallurgists are always struggling. Undoubtedly there is call for a key. As the plan for the work progressed, it soon became evident that a detailed, cook-book sort of explanation for a few diagrams would not fill the bill,—that an exposition of underlying principles was what was needed. Thus the book finally evolved into a "generalized treatment, to appear as a special monograph of the series, which would at once care for the needs of the student, the chemist, the metallurgist, or any other person confronted with a problem of so-called heterogeneous equilibrium, whether his interest be in organic, inorganic salt or metallic systems." The author has undoubtedly succeeded in putting the requisite material in his allotted

187 pages of text material, but if he expects the average "student, chemist or metallurgist" to be able to master it, he has decidedly overshot his mark.

As it stands, it is a book for the experts, though in the preface the author seems to apologize because he did not "enter the field of advanced phase theory or of philosophic argument." Even at that he is working considerably over the heads of those who are going to be the greatest users of the books of the Alloys of Iron Research Series. It is a book for experts, because the material is for the most part presented in the abstract or a generalized form; not as abstractly as Gibbs presentations by any means, but the treatment is usually too general to build up clear physical concepts. That the reader must do for himself, and he must have a considerable background of experience in that sort of thing.

In a few cases the author must have felt that he was throwing out a morsel a little too tough for the intended audience and therefore tried to "write down" to the field; he usually overdid it. For example, he uses almost two pages to explain the very simple items of mass percentage, "often called (erroneously) *weight percentage*," and mole percentage, but in the next chapter he uses only a little over one-half a page to explain a subject fully one hundred times as involved,—the conditions of thermodynamic equilibrium. He also seems to spend a great deal of time in polishing his definitions to the point of fastidiousness.

Though the title of the book and the preparatory intentions may be somewhat misleading, that does not detract from its excellence. For the well-trained physical chemist, well versed in heterogeneous equilibria, it is an excellent review and gives many new viewpoints. For the average person who will be interested in phase diagrams, this book should be labelled as a base camp in a wilderness of considerable complexity. It should be the frame work for a reading course of considerable magnitude, a place to which the explorer can return at frequent intervals to replenish his supplies, but not, it is feared, to rest. The work would be useful to a great many more people if there were more complete and specific references for outside study. This is especially necessary to help build up physical concepts by illustration of known physical phenomena.

The average person who becomes interested in phase diagrams is one who has had a certain amount of physical chemistry and perhaps thermodynamics, but is by no means an expert in heterogeneous equilibrium. He suddenly has good reason to learn more of the significance of the complex labyrinth of some ternary diagram. He soon discovers his shortcomings and decides to study up a bit. Such a person should not be advised to take this book undiluted. The reviewer would recommend that he first brush off some of the dust by reviewing portions of one of the simpler college texts on physical chemistry, Getman's perhaps. Then he should work over the applicable portions of the section on heterogeneous equilibrium in Taylor's *Treatise on Physical Chemistry*. After this "warming up" period, he should take up Marsh's Chapter I, on "Fundamentals." This chapter may then seem very simple, but that is an illusion, for the background study is essential to master all the concepts involved. The student should then jump over the long and meaty Chapter II, "Fundamentals (Continued)", and study the chapter entitled "Systems of One and Two Components." After that it is time to leave Marsh for a while. The student needs some outside work at this point to help build up concepts for the three-component system. Passing over all the pedagogical efforts in this field, there is probably nothing that will help as much in giving a person an understanding of a complicated three-component system as Rankin and Wright's outstanding article on "The Ternary System CaO–Al_2O_3–SiO_2" (Am. J. Sci. [4] **39**, 1–79 (1915). A side excursion into Findlay's *Phase Rule* might be interesting but not necessary. After the student has gone this far he can probably interpret most phase diagrams with considerable confidence and facility. If he wishes to go deeper into the subject he should now return to Marsh's Chapters IV and V on ternary systems, provided he is ready to do some serious studying. He may profitably continue into the chapter on "Conclusions," where systems of more than three components are discussed. If by this time the student is interested in the real fundamentals of the subject, he may turn to Chapter II "Fundamentals (Continued)." He will get a good review of parts of his thermodynamics and might find it profitable to refer to portions of Lewis and Randall's *Thermodynamics* and Planck's *Treatise on Thermodynamics*. In addition to this he will find some interesting discussions on the properties of non-perfect solutions and intermolecular forces. After completing this course of study the student will feel that he has been to places of considerable consequence, but the long journey is necessary if one is to get a real understanding of the material in Marsh's book. The short distance between the covers is deceptive. Do not be misled.

C. C. FURNAS.

The Optical Basis of Chemical Valence. By R. DE KRONIG. Cambridge Physical Chemistry series. 237 pp.; 67 figs. Cambridge University Press.

The modern ideas of atomic and molecular structure are discussed briefly. Most of the mathematical formulas are stated without derivation. Any other procedure is of course impossible in the space of this volume. The book best lends itself therefore to obtaining a general view of modern thought in the fields of structure of atoms and molecules as derived from spectroscopy. The nature of chemical binding and dissociation are dealt with on a modern basis. The beginning student can get a good survey of the field, and the advanced reader will enjoy the clear concise style in which the book is written. That the author has succeeded in covering the field remarkably well is shown by the chapters into which the volume is divided: I. Introduction. II. The investigation of atomic and molecular structure by means of x- and cathode rays. III. Atomic spectra and the periodic system. IV. Band spectra and chemical binding in diatomic molecules. V. Band spectra and chemical binding in polyatomic molecules. VI. Optical and thermal dissociation. Each chapter ends with a bibliography and a list of references to the original literature. A special table of the electron configuration of the elements is appended. Any reader who would use this volume as a guide to a study of modern chemical physics and follow some of the literature cited, would gain a very complete picture of this fascinating subject.

GEORGE GLOCKLER.

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